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TECHNICAL REPORT

Halogenated Explosives to Defeat Biological Agents

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September 2015

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Prepared by:
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14. ABSTRACT Objectives of this project included the preparation of novel chemical explosive compounds capable of producing biocidal products of explosion (particularly hydrogen fluoride) as well as one or more explosive formulations suitable for determination of their feasibility as effective agent defeat weapon components. Such new formulations could provide significantly better airborne-agent neutralization/defeat capabilities than existing high-explosive, thermobaric, and high-temperature incendiary payloads by employing chemical kill mechanisms with high efficiency.					
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CONVERSION TABLE

Conversion Factors for U.S. Customary to metric (SI) units of measurement.

MULTIPLY → BY → TO GET
TO GET ← BY ← DIVIDE

angstrom	1.000 000 x E -10	meters (m)
atmosphere (normal)	1.013 25 x E +2	kilo pascal (kPa)
bar	1.000 000 x E +2	kilo pascal (kPa)
barn	1.000 000 x E -28	meter ² (m ²)
British thermal unit (thermochemical)	1.054 350 x E +3	joule (J)
calorie (thermochemical)	4.184 000	joule (J)
cal (thermochemical/cm ²)	4.184 000 x E -2	mega joule/m ² (MJ/m ²)
curie	3.700 000 x E +1	*giga bacquerel (GBq)
degree (angle)	1.745 329 x E -2	radian (rad)
degree Fahrenheit	$t_k = (t^{\circ}f + 459.67) / 1.8$	degree kelvin (K)
electron volt	1.602 19 x E -19	joule (J)
erg	1.000 000 x E -7	joule (J)
erg/second	1.000 000 x E -7	watt (W)
foot	3.048 000 x E -1	meter (m)
foot-pound-force	1.355 818	joule (J)
gallon (U.S. liquid)	3.785 412 x E -3	meter ³ (m ³)
inch	2.540 000 x E -2	meter (m)
jerk	1.000 000 x E +9	joule (J)
joule/kilogram (J/kg) radiation dose absorbed	1.000 000	Gray (Gy)
kilotons	4.183	terajoules
kip (1000 lbf)	4.448 222 x E +3	newton (N)
kip/inch ² (ksi)	6.894 757 x E +3	kilo pascal (kPa)
ktap	1.000 000 x E +2	newton-second/m ² (N-s/m ²)
micron	1.000 000 x E -6	meter (m)
mil	2.540 000 x E -5	meter (m)
mile (international)	1.609 344 x E +3	meter (m)
ounce	2.834 952 x E -2	kilogram (kg)
pound-force (lbs avoirdupois)	4.448 222	newton (N)
pound-force inch	1.129 848 x E -1	newton-meter (N-m)
pound-force/inch	1.751 268 x E +2	newton/meter (N/m)
pound-force/foot ²	4.788 026 x E -2	kilo pascal (kPa)
pound-force/inch ² (psi)	6.894 757	kilo pascal (kPa)
pound-mass (lbm avoirdupois)	4.535 924 x E -1	kilogram (kg)
pound-mass-foot ² (moment of inertia)	4.214 011 x E -2	kilogram-meter ² (kg-m ²)
pound-mass/foot ³	1.601 846 x E +1	kilogram-meter ³ (kg/m ³)
rad (radiation dose absorbed)	1.000 000 x E -2	**Gray (Gy)
roentgen	2.579 760 x E -4	coulomb/kilogram (C/kg)
shake	1.000 000 x E -8	second (s)
slug	1.459 390 x E +1	kilogram (kg)
torr (mm Hg, 0° C)	1.333 22 x E -1	kilo pascal (kPa)

*The bacquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.

**The Gray (GY) is the SI unit of absorbed radiation.

EXECUTIVE SUMMARY

We undertook the preparation of novel chemical explosive compounds capable of producing biocidal products of explosion as well as an explosive formulation based on one such candidate, which would be suitable for determination of its feasibility as an effective agent defeat weapon component.

As part of this project, a literature search was conducted for novel organic energetic materials that, following detonation or deflagration to equilibrium products, would particularly include hydrogen fluoride (HF). As an alternative to *N,N*-difluoramines, such as HNFX, studied as an agent defeat ingredient in a prior DTRA-funded project, a compound containing fluorine based on C–F bond linkages was desired for comparison to the N–F source offered by HNFX.

Following consideration of many criteria that needed to be met by practical (i.e., qualify-able) explosive formulations that could generate sporicidal products of explosion, two most attractive candidates were chosen upon down selection: tris(trifluoromethyl)RDX or “TFM-RDX” ($C_6H_3F_9N_6O_6$ = 40.13% fluorine); and 1,3,5-trinitro-2,4,6-tris(trifluoromethyl)benzene ($C_9F_9N_3O_6$ = 40.99% fluorine). The latter target was an unknown compound, and several unsuccessful attempts to newly prepare it—as well as consideration of the economics of possible alternative technical approaches that might produce it—led to its abandonment, in this project, in favor of TFM-RDX.

TFM-RDX was a known compound, reported only once in prior literature, so it was prepared and better characterized for the present application, in which it was formulated into a plastic-bonded explosive analogous to PBXN-5. This research composition, “TFM-PBX-5,” was formulated as a ternary mixture (TFM-RDX + HMX + fluorinated copolymer binder) that would maximize hydrogen fluoride content in its products of explosion, thus being capable of producing 29.8 wt% HF upon detonation.

The new formulation, TFM-PBX-5, was pressed into pellets suitable in size to substitute for pellets of PBXN-5 used as the conventional booster charge in agent defeat test hardware currently in place at NSWC Indian Head. The pellets were shipped to Indian Head in order to continue this collaborative study by measuring the sporicidal efficacy (against anthrax surrogates) of highly fluorinated organic explosive formulations in comparison to conventional (CHNO-based) explosives.

OBJECTIVES

Objectives of this project included the preparation of novel chemical explosive compounds capable of producing biocidal products of explosion (particularly hydrogen fluoride) as well as one or more explosive formulations suitable for determination of their feasibility as effective agent defeat weapon components. Such new formulations could provide significantly better airborne-agent neutralization/defeat capabilities than existing high-explosive, thermobaric, and high-temperature incendiary payloads by employing chemical kill mechanisms with high efficiency.

BACKGROUND, PREMISE, AND GENERAL APPROACH

As part of this project, “Halogenated Explosives to Defeat Biological Agents,” a literature search was conducted for novel organic energetic materials—suitable for application in NSWC Indian Head’s test apparatus^{1,2} to measure sporicidal efficacy—that, following detonation or deflagration to equilibrium products, would particularly include hydrogen fluoride. The past DTRA-funded project “*N,N*-Dihaloamine Explosives as Harmful Agent Defeat Materials” at NAWCWD China Lake successfully demonstrated the feasibility of that class of compounds for agent defeat with an *N,N*-difluoramine, octahydro-3,3,7,7-tetrakis(difluoramino)-1,5-dinitro-1,5-diazocine (HNFX).³ Although its sporicidal efficacy for agent defeat was attractive ($\geq 9 \log_{10}$ -reduction of *Bt* spores in ~5 seconds), HNFX is problematic as an agent defeat weapon (ADW) main charge ingredient for a couple of reasons. It has explosive sensitivity somewhat greater than that of pentaerythrityl tetranitrate (PETN), as shown in Table 1 for samples of HNFX prepared at NAWCWD, so that explosive formulations using HNFX as the main charge most likely will behave as primary explosives, complicating their deployment in large munitions.

¹ (a) Lightstone, J.M.; Wells, C. “Development and Characterization of Prompt Agent Defeat Materials and Methods”, *2011 DTRA Basic Research Technical Review* (Springfield, VA), 26 July 2011; (b) Horn, J. et al. “Development and Characterization of Prompt Agent Defeat Materials and Methods”, *2012 DTRA Basic Research Technical Review* (Springfield, VA), 25 July 2012; (c) Lightstone, J.M. et al. “Development and Characterization of Prompt Agent Defeat Materials and Methods”, *2013 DTRA Basic Research Technical Review* (Springfield, VA), 25 July 2013; (d) Lightstone, J.M. “Development and Characterization of Prompt Agent Defeat Materials and Methods”, *2014 DTRA Basic Research Technical Review* (Springfield, VA), 30 July 2014.

² Milby, C.; Stamatis, D.; Carney, J.; Horn, J.; Lightstone, J. “Efficacy of Energetic Formulations in the Defeat of Bio Agents”, *Central States Section of the Combustion Institute Spring Technical Meeting 2012* (Dayton, OH), 23–24 April 2012; https://www.combustioninstitute.org/upload_resources/12S-86.pdf.

³ (a) Chapman, R.D. et al. “*N,N*-Dihaloamine Explosives as Harmful Agent Defeat Materials”, Final Report (DTRA Proposal #BRCALL07-A-2-0015), 31 Dec 2011; (b) Chapman, R.D. “*N,N*-Dihaloamine Explosives as Harmful Agent Defeat Materials”, *2011 DTRA Basic Research Technical Review* (Springfield, VA), 26 July 2011.

Table 1. Sensitivity of HNFX Samples Prepared at NAWCWD China Lake

Property (Method) ^a	HNFX (cryst)	HNFX (coated) ^c	PETN (typical)
ESD (NAWC) “ $E_{50} \pm s_E$ ” (mJ @ 0.02 μ F) ^b	15.1 \pm 3.0 to 79.1 \pm 25.0	125.0 \pm 49.5	10/10 No-Fires @ 250 mJ
Impact (ERL 2.5 kg) $H_{50} \pm s_H$ (cm) ^b	5.42 \pm 0.48 to 9.06 \pm 3.48	9.03 \pm 0.49 to 11.54 \pm 1.54	11–12
Friction (ABL) “ F_{50} ” (lbf) ^b	10/10 Fires @ 50 lbf	~98	195~224
^a <i>Manual of Data Requirements and Tests for the Qualification of Explosive Materials for Military Use</i> , NATO AOP-7 (Edition 2, Rev. 1), Dec 2004. ^b Parameters calculated as 50% points (Bruceton method) with standard deviations s . ^c Crystals coated with various fluorinated oils			

If sensitivity were the only issue with HNFX, problems with its utilization in ADW might not be insurmountable. Other primary explosives even more sensitive than HNFX are mass-produced and formulated on a large scale, e.g., lead styphnate with a market of tens of thousands of pounds—approaching 100,000 pounds—per year.⁴ However, in addition to its high sensitivity, production of HNFX by the current “best” method⁵ is also prohibitively expensive on a large scale, requiring expensive 4-nitrobenzenesulfonamide starting material (as well as elemental fluorine) and trifluoromethanesulfonic acid as a solvent in the final step. Thus, the cost to mass-produce HNFX and the likely high sensitivity of explosive formulations based on it make this particular difluoramine impractical to scale up for use in a fielded ADW.

As an alternative to *N,N*-difluoramines, a compound containing fluorine based on C–F bond linkages was desired for comparison to the N–F source offered by HNFX. It would be desirable for the energetic material to provide the maximum quantity of fluorine possible for an organic energetic material while still being usable in NSWC’s test apparatus. Not considered as suitable candidates for this basic research project were formulations of nonfluorinated conventional energetic materials with nonenergetic fluorinated ingredients, although some such formulations have been historically developed as explosives, e.g., LX-11 with 80:20 HMX–Viton A⁶ or the Chinese formulation “O/F,” which is HMX with 40% fluorinated rubber (F_{26–41}, essentially equivalent to Viton).⁷

Furthermore, only solid ingredients were considered as viable candidates for near-term application for agent defeat weapons because of logistic difficulties in weaponizing liquid explosives into munitions. Because of the nature of physical and chemical properties imparted by high fluorine content on organic compounds, the selection of feasible candidate compounds became very limited. High fluorine content in organic compounds tends to make them either

⁴ (a) National Library of Medicine HSDB database <http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm>; (b) Fronabarger, J.W.; Williams, M.D.; Sanborn, W.B.; Sitzmann, M.E.; Bichay, M. *SAFE Journal* **2007**, 35(1), 14.

⁵ Chapman, R.D.; Groshens, T.G. *U.S. Patent* 7,632,943 (2009).

⁶ Hoffman, D.M. *Polym. Eng. Sci.* **2003**, 43, 139.

⁷ Tongchang, Y.; Menchao, T.; Jianling, W. *J. Therm. Anal.* **1995**, 44, 1347.

chemically less reactive—i.e., like Viton or Teflon—rather than energetic if there is a significant carbon backbone to which the fluorines are bonded, or, alternatively, smaller molecules—with sufficiently high energetic constituency but also with high fluorine content—tend to have low melting points, generally being liquid at room temperature, since hydrogen bonding to typical energetic substituents, such as NO₂, is lost because of the substitution of hydrogen by fluorine. (Allowing for fluorinated energetic liquids to be tested could have opened up more opportunities for candidate materials, and some of those were preliminarily considered as well.) Table 2, below, contains several examples comparing properties of “conventional” (CHNO) energetic molecules to their polyfluorinated analogs, demonstrating the effect of lowering their melting and boiling points upon introducing high fluorine content.

One source consulted in order to choose candidate fluorinated energetic materials was a compilation of all (1516) known aliphatic fluoronitro compounds (as of 1990) which was compiled by Eugene R. Bissell (formerly of Lawrence Livermore National Laboratory), self-published and sold as a software database of compounds, methodology, and properties.⁸ In addition, several structural searches were conducted in Chemical Abstracts Service’s SciFinder[®] database in order to find all known compounds with structural features meeting the necessary criteria above, particularly fluorine content contributed by trifluoromethyl (CF₃) substituents as well as conventional energetic features such as nitramine (N–NO₂) or nitroorganic (aliphatic or aromatic C–NO₂) structural components. Another database utilized for bibliographic searching was the Defense Technical Information Center’s DTIC Online Access Controlled (DOAC), a gateway to Department of Defense (DoD) unclassified, controlled science and technology (S&T), and research and engineering (R&E) information.⁹ Yet another information resource consulted for bibliographic searching was the Department of Energy’s Information Bridge.¹⁰ These searches turned up potentially promising solid-phase candidates listed in Table 3 (following the body of this report), which also includes another difluoramine derivative besides HNFx.

An important consideration for a final downselection of candidate materials to be prepared for testing is their practicality to prepare on the scale needed (20–25 grams) and with the resources (including commercially available starting materials) available to the current project. Not necessarily all of the candidates preliminarily considered might qualify with that criterion as well, so the table lists candidates in an approximately decreasing order of overall attractiveness in terms of properties offered and practicality of preparation.

As a general class, pentafluorosulfanyl (SF₅) derivatives were also considered, as some energetic examples of this class have been prepared by researchers over the years.¹¹ However, if another criterion is assumed that compounds practical for deployed ADW must be producible and affordable at a scale of perhaps hundreds or thousands of pounds, and not merely on a small scale of grams, then reported energetic derivatives of SF₅ become less attractive as candidates.

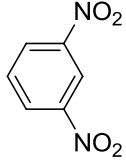
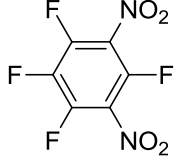
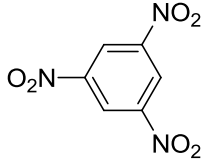
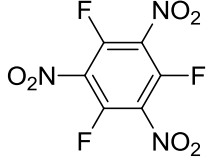
⁸ Bissell, E.R. “The Chemistry of Aliphatic Fluoronitro Compounds” [software database], Alamo CA: Eugene R. Bissell, 1990.

⁹ <https://www.dtic.mil/DOAC/home.search>

¹⁰ <http://www.osti.gov/bridge/advancedsearch.jsp>

¹¹ (a) Sitzmann, M.E.; Gilligan, W.H.; Ornellas, D.L.; Thrasher, J.S. *J. Energ. Mater.* **1990**, *8*, 352; (b) Sitzmann, M.E. *J. Fluor. Chem.* **1991**, *52*, 195; (c) Garg, S.; Shreeve, J.M. *J. Mater. Chem.* **2011**, *21*, 4787; (d) Martinez, H.; Zheng, Z.; Dolbier, W.R. “Synthesis of Novel Furazan-Based Energetic Materials Containing an SF₅ Group”, *20th Winter Fluorine Conference* (St. Pete Beach, FL), 9–14 January 2011, FLUO-10.

Table 2. Phase transitions of selected polyfluorinated vs. conventional (CHNO) nitro compounds

Structure	m.p. (°C) [ref]		b.p. (°C) / <i>P</i> (torr) [ref]	
CH ₃ NO ₂	−28°	[a]	101°	[a]
CF ₃ NO ₂			−33°	[b]
NO ₂ CH ₂ CH ₂ NO ₂	40°	[c]	135° / 5	[c]
NO ₂ CF ₂ CF ₂ NO ₂	−33°	[d]	57° / 750	[e]
(CH ₃) ₂ N−NO ₂	58°	[f]	187° / 759	[g]
(CF ₃) ₂ N−NO ₂			15°	[h]
(CH ₃ CH ₂) ₂ N−NO ₂			203°	[i]
(CF ₃ CH ₂) ₂ N−NO ₂	1°	[j]	43°	[j]
[CF(NO ₂) ₂ CH ₂ O] ₂ CH ₂	14°	[k]	120° / 0.3	[k]
[CF(NO ₂) ₂ CH ₂ O] ₂ CF ₂	−17°	[l]	100° / 2	[m]
	90°	[n]	292°	[o]
	(liquid)	[p]	228°	[p]
	123°	[q]		
	87°	[r]		

[a] Toops, E.E. Jr. *J. Phys. Chem.* **1956**, 60, 304.[b] Ginsburg, V.A.; Medvedev, A.N.; Lebedeva, M.F.; Vasil'eva, M.N.; Martynova, L.L. *Zh. Obshch. Khim.* **1967**, 37, 611.[c] Smith, A.E.W. *U.S. Patent* 2384047 (1945).

[d] Frazer, J.W.; Sanborn, R.H. "Purification and Physical Properties of 1,1,2,2-Tetrafluorodinitroethane", Univ. Calif. Radiation Laboratory (Livermore) Report UCRL-4978, 1957.

[e] Hass, H.B. *U.S. Patent* 2447504 (1948).[f] Emmons, W.D.; Freeman, J.P. *J. Am. Chem. Soc.* **1955**, 77, 4387.[g] van Romburgh, P. *Rec. Trav. Chim.* **1884**, 3, 7.

Table 2 (cont.). Phase transitions of selected polyfluorinated vs. conventional (CHNO) nitro compounds

- [h] Medvedev, A.N.; Smirnov, K.N.; Dubov, S.S.; Ginsburg, V.A. *J. Gen. Chem. USSR* **1968**, 38, 2378.
[i] Chute, W.J.; Dunn, G.E.; Mackenzie, J.C.; Myers, G.S.; Smart, G.N.R.; Suggitt, J.W.; Wright, G.F. *Can. J. Res. B* **1948**, 26, 114.
[j] Meen, R.H.; Wright, G.F. *J. Org. Chem.* **1954**, 19, 391.
[k] Marcus, H.J. *Preprints of Papers – American Chemical Society, Division of Fuel Chemistry* **1968**, 12(2), 56.
[l] Eremenko, L.T.; Oreshko, G.V.; Fadeev, M.A.; Garanin, V.A. *Proc. Internat. Pyrotech. Seminar* **1998**, 24, 217.
[m] Eremenko, L.T.; Oreshko, G.V.; Fadeev, M.A. *Bull. Acad. Sci. USSR (Div. Chem. Sci.)* **1989**, 101.
[n] Bachman, G.B.; Vogt, C.M. *J. Am. Chem. Soc.* **1958**, 80, 2987.
[o] Jaeger, F.M. *Z. Anorg. Allg. Chem.* **1917**, 101, 1.
[p] Coe, P.L.; Jukes, A.E. *Tetrahedron* **1968**, 24, 5913.
[q] Foster, R. *Tetrahedron* **1960**, 10, 96.
[r] Shaw, G.C. III; Seaton, D.L. *J. Org. Chem.* **1961**, 26, 5227.

The “starting material” used for virtually all of the potentially interesting SF₅ candidates has been SF₅Cl (and then synthetic sequences typically involve several steps beyond the use of SF₅Cl). However, SF₅Cl is no longer commercially available in the USA except via vendors who would outsource it from overseas or custom-manufacture it. The latter option appears to be prohibitively expensive even for R&D testing at a scale of kilograms. The “friendliest” foreign country that has a vendor who stocks it is Germany (ABCR in Karlsruhe), where it costs about \$847 for 25 grams at the time of this writing.¹² Therefore, reported energetic derivatives of SF₅ dependent on SF₅Cl for synthesis have been discounted as candidates for testing in this project.

Other important criteria for fluorinated energetic materials for agent defeat are the fluorine content of the molecule—to maximize sporicide (hydrogen fluoride) concentration in the gaseous products of explosion—and its oxygen balance, which contributes to its effectiveness as an energetic material undergoing detonation or deflagration. Oxygen balance Ω (relative to CO₂) for CHNOF-based compounds of composition C_aH_bN_cO_dF_e is calculated according to the equation

$$\Omega(\%) = -1599.94(2a + b/2 - d - e/2)M_w^{-1}$$

where M_w is the compound’s molecular weight. For comparison, the oxygen balance of trinitrotoluene (C₇H₅N₃O₆) is $\Omega = -74.0\%$; compounds with a near-zero or less negative oxygen balance—i.e., better balanced to CO₂—should perform better as explosives; CL-20 has $\Omega = -10.95\%$. Of course, oxygen balance alone does not guarantee a compound’s energetic character: obviously, the oxygen balance of carbon dioxide (CO₂) is zero—“better” than CL-20’s—but it is not explosive.

Therefore, also important for calculations of explosive performance (particularly of formulations that incorporate PBXN-5 booster charges as in NSWC’s test configuration) and of the composition of final products of detonation or deflagration are *enthalpies (heats) of formation* of molecules, from which enthalpies of reaction can be derived. These are also given in the table below, estimated here by subtracting predicted enthalpies of vaporization¹³

¹² http://shop.abcr.de/abcrestore/product_information.aspx?product_id=18067

¹³ Obtained from each compound’s SciFinder database entry, which calculates $\Delta H_{\text{vap}}^{\text{theor}}$ using Advanced Chemistry Development (ACD/Labs) Software v11.02 (©1994–2012 ACD/Labs), which uses an algorithm based on a compound’s chemical class and its normal boiling point

($\Delta H_{\text{vap}}^{\text{theor}}$) from the compounds' predicted *gas-phase* enthalpies of formation, calculated using the MOPAC2009 quantum chemistry software package¹⁴—which uses PM6, the latest parameterization of Dewar and Thiel's NDDO method—following conformational energy minimization of the compounds in Chem3D Pro 12.0,¹⁵ which uses a modified version of Allinger's MM2 force field method and produces a MOPAC input file. While a more accurate estimation of a solid-phase enthalpy of formation would be given by subtracting a compound's *enthalpy of sublimation* from its gas-phase enthalpy of formation,¹⁶ enthalpies of sublimation are not as conveniently computed as enthalpies of vaporization which are available in the SciFinder database. (The differences between those enthalpies would be a solid-phase compound's enthalpy of fusion.) However, the enthalpies of vaporization were deemed to offer a sufficient approximation of the enthalpy of sublimation for the purpose of selecting fluorinated energetic candidates to generate hydrogen fluoride for agent defeat applications. A specific comparison of these parameters can be seen for RDX: its enthalpy of vaporization estimated in SciFinder is 105.06 ± 3.0 kJ/mol; its measured enthalpy of sublimation has been reported in the range of 109.0–134.7 kJ/mol¹⁷ (i.e., reasonably approximated by the estimated enthalpy of vaporization); and its measured enthalpy of fusion has been reported in the range of 35.65–37.66 kJ/mol.^{18,19}

A very attractive candidate among those with fluorine present only in C–F bonds appears to be compound **1** (Table 3), which may be called tris(trifluoromethyl)RDX (“TFM-RDX”), which has a relatively straightforward (although not trivial) synthesis, relatively high fluorine content (among the qualified energetic candidates), good physical properties, and usable energetic content.

Other difluoramines besides HNFX were considered as alternative main charge ingredients for ADW on the hypothesis that it is the chemical nature of detonation by organic difluoramines—e.g., the formation of transient, highly reactive and sporicidal fluorinated intermediates—that produced the successful sporicidal result exhibited by HNFX.³ Compound **2**, 1,1,4,4-tetrakis(difluoramino)cyclohexane (TDCH), is potentially attractive in having a straightforward one-step synthesis (Figure 1)—from a commercially available organic starting material—less expensive than that of HNFX, adequate physical properties, and high fluorine content—all of it present as energetic NF_2 , so its intrinsic energy is not conspicuous in its enthalpy (heat) of formation parameter in comparison to those of other candidates containing oxygen as an oxidizing element.

[“ACD/Boiling Point (Version 12.0 for Microsoft Windows) User's Guide,” Advanced Chemistry Development, Inc., 2008].

¹⁴ MOPAC2009™, J.J.P. Stewart, Stewart Computational Chemistry, Version 11.038W; <http://OpenMOPAC.net>. Dr. Stewart is gratefully acknowledged for a key to utilize a copy of MOPAC2009 used for these calculations.

¹⁵ <http://chembionews.cambridgesoft.com/FeatureClips/Default.aspx?featureclipID=95>

¹⁶ Rice, B.M.; Pai, S.V.; Hare, J. *Combust. Flame* **1999**, *118*, 445.

¹⁷ Cundall, R.B.; Palmer, T.F.; Wood, C.E.C. *J. Chem. Soc. Faraday Trans. 1* **1978**, *74*, 1339; and references therein.

¹⁸ Hall, P.G. *Trans. Faraday Soc.* **1971**, *67*, 556.

¹⁹ Domalski, E.S.; Hearing, E.D. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1.

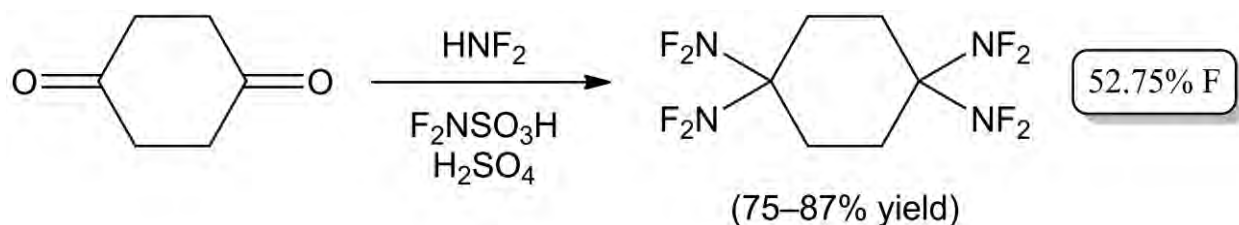
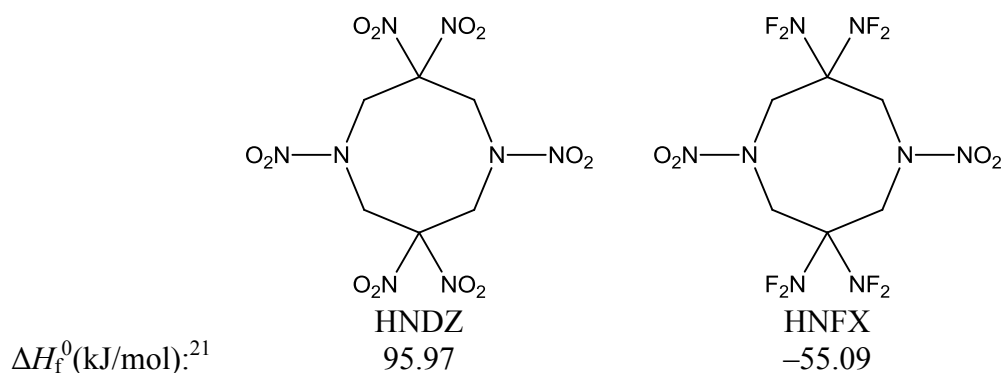


Figure 1. Synthesis of 1,1,4,4-tetrakis(difluoramino)cyclohexane (TDCH)

The reaction whose enthalpy defines compounds' enthalpy of formation—their formation from the corresponding elements—will more likely be thermodynamically favorable for *fluorine-containing* organic compounds because of the high reactivity of elemental fluorine, being greater than that of elemental oxygen; thus, their enthalpies of formation (ΔH_f^0) are likely to appear more negative or less positive than similarly oxygen-balanced *CHNO* compounds, even though the fluorinated compounds' enthalpies of *detonation or combustion* may be more favorable, i.e., more energetic. Thus, for an equivalently oxygen-balanced “formulation,” compare the enthalpy of formation of two moles of hydrogen fluoride from the elements ($\text{H}_2 + \text{F}_2$), $\Delta H_f^0(2\text{HF}) = -545.09 \text{ kJ/mol}$, to that of one mole of water, $\Delta H_f^0(\text{H}_2\text{O}) = -285.83 \text{ kJ/mol}$;²⁰ this difference in the compounds' enthalpies of formation (HF vs. H_2O) will be reflected in enthalpies of combustion/detonation reactions that produce either product:

$$\Delta H_f(\text{reaction}) = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

will be more favorable (negative) with fluorinated product HF than with water. See an example of comparative enthalpies of formation of the two classes of compounds (NF_2 vs. NO_2) in the cases of HNF_X vs. HNDZ both estimated by the same computational method.²¹



Therefore, 1,1,4,4-tetrakis(difluoramino)cyclohexane (TDCH) has a very attractive estimated heat of formation. However, in light of the high explosive sensitivity of HNF_X (Table 1), the sensitivity of TDCH (**2**), still a difluoramine, must also be considered. Unfortunately, reports of the impact sensitivity of TDCH show it also to be significantly more sensitive than

²⁰ Chase, M.W. Jr. “NIST–JANAF Thermochemical Tables” (4th ed.), Springer-Verlag, 1998.

²¹ Fan, X.-W.; Ju, X.-H.; Xiao, H.-M. *J. Hazard. Mater.* **2008**, *156*, 342.

PETN, as is HNF_X: H_{50} at 0.5 kg has been reported as 5–10 cm,²² which may be a questionable value in comparison to another report of H_{50} at 1 kg being 10–20 cm.²³ Despite this discrepancy, these compare to H_{50} at 0.5 kg for PETN being 60–80 cm,²⁴ so TDCH is certainly more sensitive than PETN. The relatively high impact as well as electrostatic discharge sensitivities of TDCH are corroborated by other limited-distribution reports.

This sensitivity problem that HNF_X and TDCH have in common prompted a review of essentially all sensitivity data on hundreds of difluoramine derivatives that were prepared during “Project Principia,”²⁵ many of which were conveniently collected in an extensive handbook.²⁶ It seemed to be a common finding that organic difluoramines as a class were generally too sensitive when the compounds’ NF₂ content was high and the difluoramine constituted a major component of a formulation—as would be necessary for explosive formulations to generate significant bio-cidal product (HF) for the present application. Thus, such formulations tended to have properties of primary explosives and were deemed too sensitive for rocket propellant applications in the past. Entire projects and conferences were devoted to the sensitivity problems that difluoramines exhibited,²⁷ and attempts to desensitize these ingredients were not usefully successful.²⁸

Even if difluoramine ingredients’ sensitivity properties—being technologically manageable for formulation as primary explosives—were deemed acceptable for agent defeat weapons, the synthetic methodology to prepare such compounds poses a different technological challenge. The synthetic transformation of difluoramination of ketones by difluoramine (HNF₂)²⁹ is a specialized, hazardous process that is not likely to become scalable to more than a very few kilograms per batch. Even a production process of that scale would require facilities that were available at Aerojet or Rocketdyne, for example, during Project Principia but are no longer present at any chemical manufacturing facility in this country. Restoring the infrastructure for such specialized production at large scale (even tens of kilograms) is probably beyond the resources of a research and development program. It may be concluded, therefore, that organic difluoramines as a class are *impractical* to adopt as main charges of agent defeat weapons.

Yet another criterion comes into play in selecting ingredients that are feasible for formulation into deployed explosive charges for agent defeat (although actually for any purpose): explosive formulations must pass testing criteria specified by NAVSEA Instruction 8020.5C “Qualification and Final (Type) Qualification Procedures for Navy Explosives (High Explosives,

²² Hill, M.E.; Brauman, S.K.; Bell, R.A. “Compilation and Review of Data on the Sensitivity and Stability of NF Compounds: A Handbook”, March 1967, p. 151; AD379931 (Approved for public release).

²³ Dinwoodie, A.; Grigor, J. *U.S. Patent* 3,624,155 (1971).

²⁴ Fordham, S. “High Explosives and Propellants” (Second Edition), New York: Pergamon, 1980, p. 71.

²⁵ Davenas, A. *J. Propul. Power* **2003**, *19*, 1108.

²⁶ Hill, M.E.; Brauman, S.K.; Bell, R.A. “Compilation and Review of Data on the Sensitivity and Stability of NF Compounds: A Handbook”, March 1967; AD379931 (Approved for public release).

²⁷ Hill, M.E. “Review and Evaluation of NF Sensitivity Problems”, March 1967; AD382934 (Approved for public release).

²⁸ Brown, J.A.; Coburn Jr., J.F.; Collins, M. “Desensitization of Available High-Energy NF Compounds”, December 1966; AD379575 (Approved for public release).

²⁹ Chapman, R.D.; Groshens, T.G. *U.S. Patent* 7,563,889 (2009).

Propellants, Pyrotechnics and Blasting Agents).”³⁰ Procedures specified by NAVSEAINST 8020.5C include testing, such as the gap test, following accelerated aging at temperatures up to 70 °C (Figure 2). Thus, qualification testing requires that solid explosive ingredients must not melt below 70 °C. (The lowest-melting common explosive ingredient in qualified ordnance is trinitrotoluene, TNT, which has a specified minimum melting point of 80.20 °C.) With this additional criterion, all candidates in Table 3 with melting points below 70 °C must be discounted from consideration as viable explosive ingredients for ADW. This leaves only compounds **1**, **6**, and probably **9** as viable candidates.

Compound **6**, however, has a rather unwieldy synthesis, requiring several steps for its preparation but only offering properties otherwise very similar to those of compound **1**.

The effect of added CF₃—as in TFM-RDX (**1**) in comparison to RDX—on explosive sensitivity should be evaluated, since such properties imparted by high NF₂ content have now precluded that class of compounds as candidates. While not many examples are available in which explosive sensitivities have been measured for both a conventional (CHNO) energetic material as well as the corresponding structure with one or more added CF₃ substituents, a couple of them have been reported. *N*-Methyl-*N*-(2,2,2-trinitroethyl)nitramine is a fairly sensitive explosive with impact sensitivity reported as H_{50} (ERL 2.5 kg) = 9 cm;³¹ structurally adding CF₃ to the methyl substituent yields *N*-(2,2,2-trifluoroethyl)-*N*-(2,2,2-trinitroethyl)nitramine, which has H_{50} (2 kg) >100 cm.³² Tetryl (*N*-methyl-*N*-nitroaniline) has impact sensitivity H_{50} (ERL 2.5 kg) = 27–32 cm where the analogous derivative with added CF₃, *N*-nitro-*N*-(2,2,2-trifluoroethyl)aniline, shows H_{50} (ERL 2.5 kg) = 156 cm.³³ Thus, the addition of CF₃ substituents to energetic structures, including nitramines, has a favorable effect in lowering sensitivity relative to conventional energetics, and TFM-RDX (**1**) should therefore have acceptable sensitivity, better than that of RDX.

A tabulation of prospective liquid fluorinated energetic materials was also developed (Table 4)—arising from the preliminary selection of candidates based only on structural criteria—which could be evaluated for further downselection of liquid ingredients should they ever become of interest.

³⁰ https://www.neco.navy.mil/upload/N00164/N0016410RJN56000310RJN56_0003_att.pdf

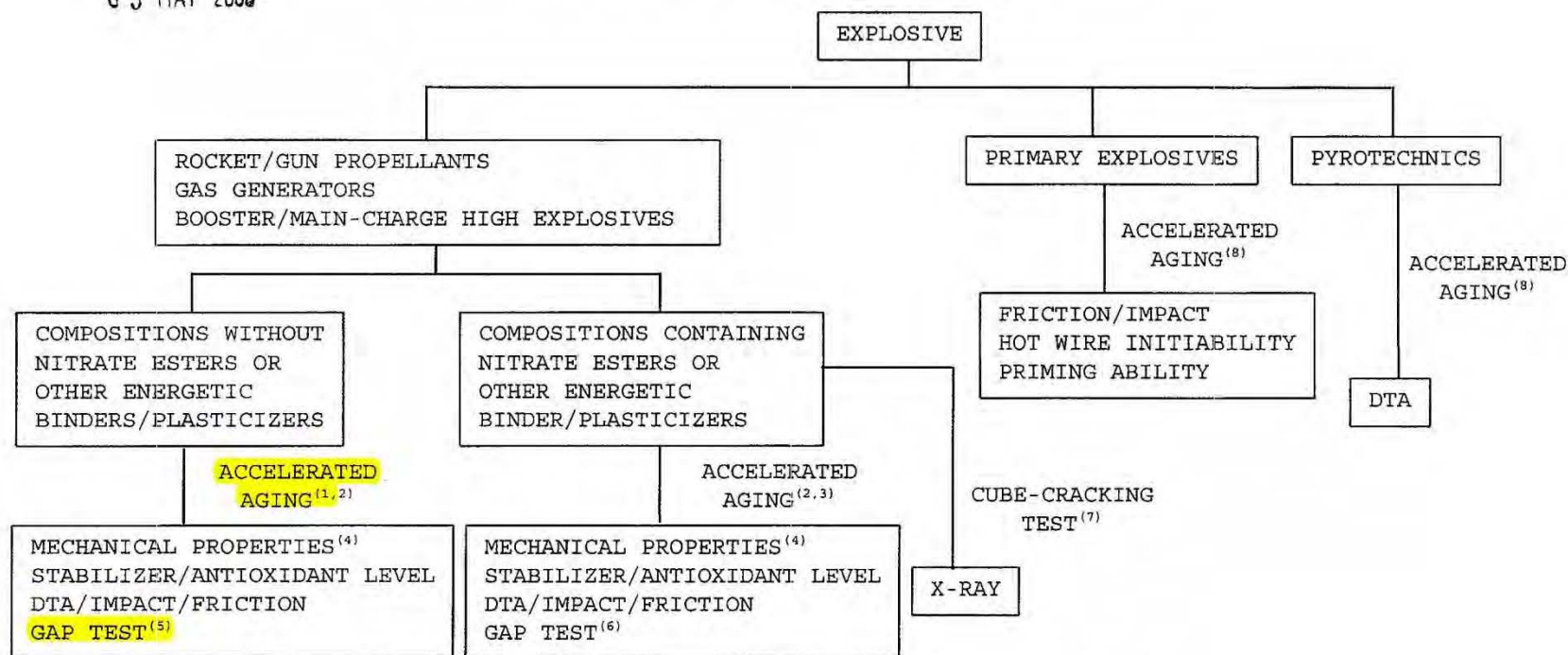
³¹ Kamlet, M.J. *Proc. Int. Det. Symp.* **1976**, 6, 312.

³² Frankel, M.B. *U.S. Patent* 3,399,235 (1968).

³³ Schmidt-Collerus, J.J.; Gray, D.N. *U.S. Patent* 3,562,333 (1971).

05 MAY 2000

FIGURE 2. AGING PROTOCOL FOR SOLID EXPLOSIVES



⁽¹⁾ 60°C - 1,2,4,6,8 MONTHS, SEALED CONTAINERS
 70°C - 1,2,4,6 MONTHS, SEALED CONTAINERS
 25°C, 30%RH - UNTIL FINAL (TYPE) QUAL

⁽²⁾ COMPOSITIONS BASED ON POLYESTER BINDERS
 WILL BE AGED UNDER CONTROLLED HUMIDITY
 (30%RH)

⁽³⁾ 50°C - 1,3,6,9,12 MONTHS, SEALED CONTAINERS
 60°C - 1,2,4,6,8 MONTHS, SEALED CONTAINERS
 25°C, 30%RH - UNTIL FINAL (TYPE) QUAL

⁽⁴⁾ HIGH RATE COMPRESSIVE STRENGTH FOR GUN
 PROPELLANTS. ALL OTHERS UNIAXIAL AT
 THREE TEMPERATURES.

⁽⁵⁾ 60°C - 8 MONTHS
 70°C - 6 MONTHS
 25°C, 30%RH - UNTIL FINAL (TYPE) QUAL
 GUN PROPELLANTS EXCLUDED

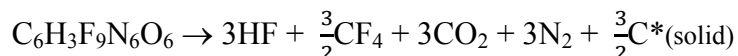
⁽⁶⁾ 50°C - 12 MONTHS
 60°C - 8 MONTHS
 25°C, 30%RH - UNTIL FINAL (TYPE) QUAL
 GUN PROPELLANTS EXCLUDED

⁽⁷⁾ 60°C
 3" CUBE FOR BOOSTER COMPOSITION
 6" CUBE FOR OTHERS
 GUN PROPELLANTS EXCLUDED

⁽⁸⁾ 70°C - 6,12 MONTHS, SEALED
 CONTAINERS
 25°C, 30%RH - UNTIL FINAL (TYPE)
 QUAL

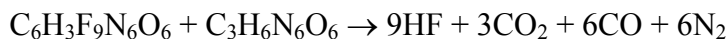
NOTE: UNLESS OTHERWISE STATED, NO
 HUMIDITY CONTROL

Candidate Finalists. Compound **1**, tris(trifluoromethyl)RDX, appeared to be the most attractive candidate encountered, in terms of all properties, including fluorine content, energetics, physical properties, and feasibility of preparation. This was chosen as the first compound pursued for experimental testing in this project. Some consideration needed to be given to its formulation with a co-ingredient, however. By itself, TFM-RDX (**1**)—with an empirical formula of $C_6H_3F_9N_6O_6$ —is deficient in hydrogen with respect to conversion of all its contained fluorine to hydrogen fluoride. Calculations of explosive performance (particularly product composition) of TFM-RDX were carried out using Cheetah 6.0 code by estimating a density of TFM-RDX, which had not been reported as experimentally measured, along with the estimated heat of formation given in Table 3. The enhancement of density imparted by substitution of hydrogen by CF_3 in a cyclic nitramine can be seen by comparison of the experimental density of tetrakis-(trifluoromethyl)bicyclo-HMX ($2.184\text{ g}\cdot\text{cm}^{-3}$)³⁴ to that of unsubstituted bicyclo-HMX ($1.861\text{ g}\cdot\text{cm}^{-3}$).³⁵ The density of TFM-RDX (**1**), needed for Cheetah calculations, was preliminarily estimated by adding three-quarters of the overall enhancement of those four CF_3 groups ($0.323\text{ g}\cdot\text{cm}^{-3}$) to the known density of RDX: $\rho(\text{TFM-RDX}) \sim 1.816 + \frac{3}{4}(0.323) \approx 2.06\text{ g}\cdot\text{cm}^{-3}$. Then Cheetah predicted the stoichiometry of detonation of TFM-RDX as a pure explosive to be approximately

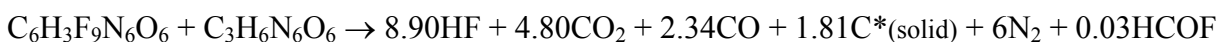


Thus, the products were estimated to contain only 13.95 wt% HF, since much of the fluorine is “tied up” as carbon tetrafluoride (CF_4), not expected to be sporicidal against biological agents.

As a possible co-ingredient, an equimolar formulation of TFM-RDX with simple RDX (65.7 wt% TFM-RDX) offers a *theoretical* oxygen balance that could completely convert all fluorine to hydrogen fluoride:



Cheetah calculations predicted that the detonation behavior of even this formulation will be more complex, however, with an approximate stoichiometry of



Still, the product composition contains 27.48 wt% HF—higher than from pure TFM-RDX explosive—because 99% of fluorine is converted to HF. Therefore, consideration needed to be given to the nature and composition of a formulation based on TFM-RDX (**1**) in order to maximize hydrogen fluoride product while maintaining adequate explosive performance.

Candidate **9**, 1,3,5-trinitro-2,4,6-tris(trifluoromethyl)benzene, was conceptually attractive with respect to properties; however, it is an unreported compound and so would require a new synthesis. It might potentially have been straightforwardly tractable via nitration of known, commercially available 1,3,5-tris(trifluoromethyl)benzene, however, since nitration between the meta CF_3 groups of 3,5-bis(trifluoromethyl)phenol has been demonstrated,³⁶ and double nitration between similarly sterically hindered meta sites of 1,3,5-tris(*tert*-butyl)benzene has been

³⁴ Koppes, W.M.; Chaykovsky, M.; Adolph, H.G.; Gilardi, R.; George, C. *J. Org. Chem.* **1987**, *52*, 1113.

³⁵ Gilardi, R.; Flippen-Anderson, J.L.; Evans, R. *Acta Cryst. Sect. E* **2002**, *58*, o972.

³⁶ Shibuya, K.; Miura, T. *U.S. Patent* 7,163,944 (2007).

achieved.³⁷ Its melting point should be acceptable, as the melting point of the nonfluorinated analog, 1,3,5-trimethyl-2,4,6-trinitrobenzene, is 232 °C,³⁸ and that of 1,3,5-trifluoro-2,4,6-trinitrobenzene (without hydrogen bonding and with lone fluorine substituents instead of larger CF₃ groups) is 87 °C.³⁹ Of course, lacking hydrogen, compound **9** would need to be formulated with a hydrogen-containing co-ingredient in order to generate hydrogen fluoride, similarly to hydrogen-deficient **1**. Since realistic explosive formulations tend to need binders anyway, this is not necessarily a drawback to its structure.

RESULTS

Attempts to prepare 1,3,5-trinitro-2,4,6-tris(trifluoromethyl)benzene (9). In parallel with efforts to develop an improved preparation of TFM-RDX (**1**), described below, the unprecedented target structure **9** was pursued. It was hoped that a straightforward, though possibly non-obvious, nitration of commercially available 1,3,5-tris(trifluoromethyl)benzene (**18**) would prove feasible. The inductive effect alone from three trifluoromethyl groups should not preclude trinitration of the aromatic ring, since trinitration of similarly inductively deactivated 1,3,5-trifluorobenzene has been demonstrated using fuming nitric plus sulfuric acids (152–156 °C).⁴⁰ Also, the steric effect of two meta-oriented trifluoromethyl groups does not preclude nitration of the common ortho carbon, demonstrated in nitration of 3,5-bis(trifluoromethyl)phenol by nitric acid/acetic acid, although the yield for the single nitration was under 30% after 43 hours (room temperature).³⁶

In anticipation of the significant inductive and steric deactivation expected to be imparted by three trifluoromethyl groups in reactant **18**, the nitrating system chosen to try would utilize *in situ* nitronium (NO₂⁺) species activated by a superacid. For example, nitration of 1,3-dinitrobenzene to 1,3,5-trinitrobenzene (66% yield) was achieved with nitronium tetrafluoroborate in fluorosulfonic acid (150 °C).⁴¹ 1,3,5-Trifluorobenzene could also be dinitrated by two equivalents (trinitration was not attempted) of nitronium tetrafluoroborate in triflic acid (70 °C), which generates nitronium triflate *in situ* upon evolution of BF₃.⁴² The superacidic solvent generates protonitronium ion (NO₂H²⁺) to some extent, a nitrating species even more powerful than nitronium ion. The specific nitrating system chosen here to test on reactant **18** is nitric acid–triflic anhydride, which generates nitronium triflate *in situ* and consumes hydronium triflate (H₃O⁺CF₃SO₃[−]), the initial by-product, to form more triflic acid; this reagent system was generally used by Olah et al. with nitromethane or nitroethane as a cosolvent.⁴³



A potential complication with this approach toward nitration of tris(trifluoromethyl)benzene (**18**) in a superacid was reported only recently: Klumpp and co-workers have claimed

³⁷ Myhre, P.C.; Beug, M.; James, L.L. *J. Am. Chem. Soc.* **1968**, *90*, 2106.

³⁸ Risch, N. *Chem. Ber.* **1985**, *118*, 4849.

³⁹ Shaw, G.C. III; Seaton, D.L. *J. Org. Chem.* **1961**, *26*, 5227.

⁴⁰ Koppes, W.M.; Adolph, H.G.; Sitzmann, M.E. *U.S. Patent* 4,173,591 (1979).

⁴¹ Olah, G.A.; Lin, H.C. *Synthesis* **1974**, 444.

⁴² Olah, G.A.; Laali, K.K.; Sandford, G. *Proc. Nat. Acad. Sci. USA* **1992**, *89*, 6670.

⁴³ Olah, G.A.; Reddy, V.P.; Prakash, G.K.S. *Synthesis* **1992**, 1087.

that **18** spontaneously (over 4 hours) converts to 3,5-bis(trifluoromethyl)benzoic acid via protolytic defluorination of CF₃ in fluorosulfonic acid–chloroform (FSO₃H–CHCl₃) solvent (Figure 3).⁴⁴

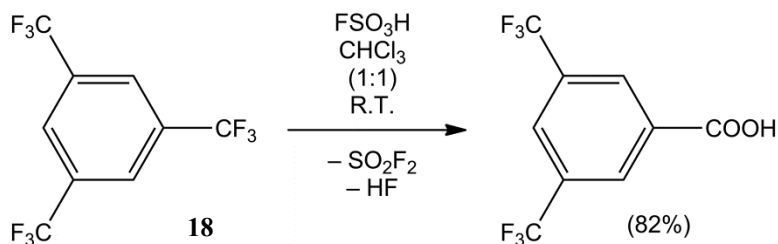


Figure 3. Reported protolytic defluorination of tris(trifluoromethyl)benzene (**18**) by a superacid⁴⁴

In contrast, however, Wang and Hu have reported that electronegatively substituted (trifluoromethyl)benzenes are not susceptible to such protolytic defluorination in triflic acid; even 4-(trifluoromethyl)propiophenone (ethyl phenyl ketone) does not undergo C–F cleavage.⁴⁵ The prospect of this complication in our proposed system was tested with a solution of **18** in triflic acid (with minor CD₂Cl₂ cosolvent). There was *no* discernable evidence of such reaction after 20 hours at ambient temperature. The proposed nitration was therefore attempted. Unfortunately, there appeared to be no significant reaction of **18** with nitronium triflate in triflic acid (formed from nitric acid–triflic anhydride), with nitromethane-*d*₃ cosolvent, even after 11 days at ambient temperature. Since the nitronium triflate–triflic acid system had been used by Olah et al. at 70 °C as well,⁴² our reaction of **18** was raised to 70 °C, but 3 days at this temperature showed only minor changes in the reaction mixture (according to multinuclear NMR), not necessarily consistent with the desired nitration.

Another modification of the system was considered, therefore, based on an observation that lanthanide(III) triflates may act as Lewis acid catalysts in nitrations of aromatic substrates in the presence of perfluoroalkanesulfonic acids.⁴⁶ For example, nitration of chlorobenzene by nitric acid with the catalyst system perfluorooctanesulfonic acid (PFOH)–ytterbium perfluorooctanesulfonate (110 °C) produced chlorotrinitrobenzene in 99% yield (24 hours). However, the potential effect of this new catalyst system on the undesired transformation of protolytic defluorination of **18** was also tested. A sample of 1,3,5-tris(trifluoromethyl)benzene (**18**) in triflic acid plus ytterbium(III) triflate (5 mol%) and nitromethane-*d*₃ cosolvent showed no appreciable change (according to multinuclear NMR) after 2½ hours at room temperature. However, after 20 hours at 70 °C, significant changes *were* seen, consistent with formation of a species like 3,5-bis-(trifluoromethyl)benzoic acid (as reported by Klumpp and co-workers⁴⁴), including a new ¹³C NMR absorption at δ 160(s), likely a carbonyl carbon. Changes in the aromatic region of the ¹H NMR spectrum indicated only ~73 mol% of starting material **18** remaining. Thus, the harsh conditions of this superacid system at this elevated temperature appeared to be incompatible with reactant **18**.

The proposed Yb(OTf)₃-catalyzed nitration of **18** was attempted at a lower temperature, therefore, in hopes of alleviating the complication of the side reaction. Fortunately, any evidence

⁴⁴ Kethe, A.; Tracy, A.F.; Klumpp, D.A. *Org. Biomol. Chem.* **2011**, *9*, 4545.

⁴⁵ Wang, F.; Hu, J. *Chin. J. Chem.* **2009**, *27*, 93.

⁴⁶ Yi, W.-B.; Cai, C. *J. Energ. Mater.* **2007**, *25*, 129.

of protolytic defluorination, if present, was negligible after 4 days at 48 °C (CD₃NO₂ cosolvent); unfortunately, neither was there evidence of any appreciable nitration of the substrate. It may be tentatively concluded, therefore, that direct nitration of **18** is too highly deactivated by the collective inductive and steric effects of the three trifluoromethyl substituents—which would become worse with any successive introductions of nitro groups—until harsher conditions would introduce the competing reaction of protolytic defluorination.

An alternative synthetic route to desired product **9** may still be envisioned (Figure 4). 2,4,6-Trinitro-1,3,5-benzenetricarboxylic acid (trinitrotrimesic acid) is a known compound, prepared by trinitration of 1,3,5-trimethylbenzene (mesitylene) with mixed acid followed by oxidation of the methyl substituents to carboxylic acids with potassium permanganate.⁴⁷ Trinitrotrimesic acid might undergo fluorination of the carboxylic acid substituents to trifluoromethyl groups on reaction with sulfur tetrafluoride (SF₄), analogous to the fluorination of simple trimesic acid to 1,3,5-tris(trifluoromethyl)benzene (**18**).⁴⁸ (However, **18** is alternatively accessible via catalyzed trimerization of commercially available 1,1,1-trifluoropropyne.⁴⁹)

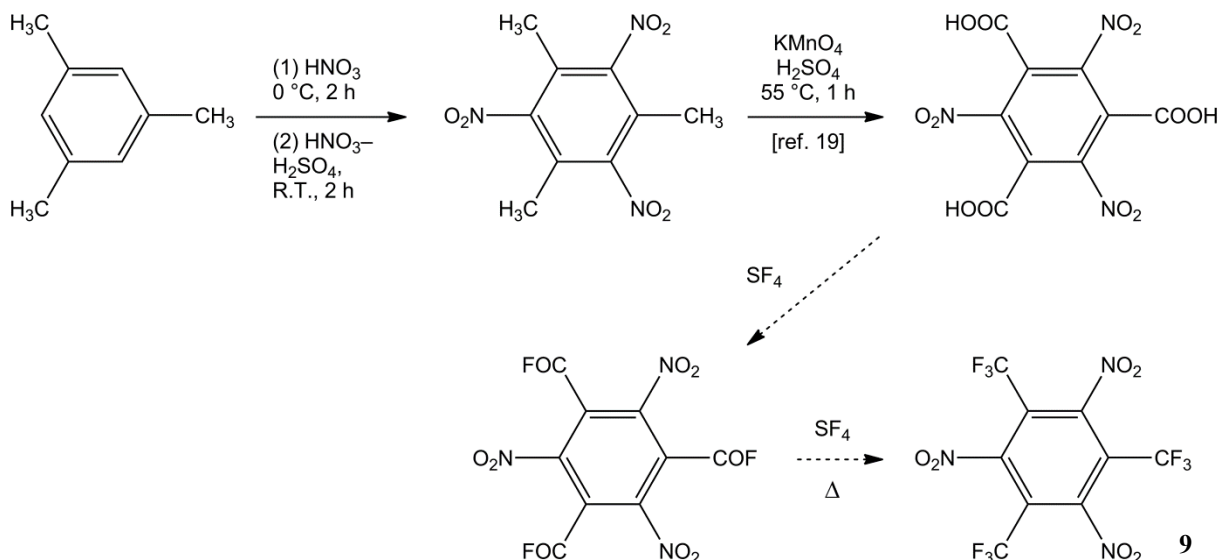


Figure 4. Conceivable alternative route to trinitrotris(trifluoromethyl)benzene (**9**)

Although this may be a technically feasible way to prepare desired product **9**, there are drawbacks that make this approach tentatively impractical. The yield of trinitrotrimesic acid precursor is only about 29% by the published route.⁴⁷ Also, the fluorinating agent, hazardous sulfur tetrafluoride gas, while commercially available, is relatively expensive for a reagent potentially required in bulk.⁵⁰ There may be technical complications with the proposed reaction as well, since further fluorination of the initial acyl fluoride intermediate—via electrophilic attack by SF₄

⁴⁷ Frankel, M.B.; Rowley, G.L. *U.S. Patent* 3,553,253 (1971).

⁴⁸ Scholz, M.; Roesky, H.W.; Stalke, D.; Keller, K.; Edelmann, F.T. *J. Organomet. Chem.* **1989**, 366, 73.

⁴⁹ Garcia, J.J.; Sierra, C.; Torrens, H. *Tetrahedron Lett.* **1996**, 37, 6097.

⁵⁰ A price quote from one source, Matheson Tri-Gas, was \$475/lb for a 90-lb cylinder.

to form fluorocarbenium ions as $-C^+F(OSF_3)$ substituents⁵¹—on to trifluoromethyl might well still be sterically deactivated by the ortho trifluoromethyl groups. This complication makes the practicality (including affordability) of the full sequence somewhat questionable.

It should also be kept in mind that prospective ingredient **9** still would require a co-ingredient in order to generate hydrogen fluoride for agent defeat, as it lacks any hydrogen itself. For these reasons—following the experimental difficulties encountered in its preparative attempts so far—the viability of this unknown compound, trinitrotris(trifluoromethyl)benzene (**9**), as a practical candidate for an ADW ingredient should be reconsidered. Thus, for the current project, this target was abandoned in favor of still-attractive tris(trifluoromethyl)RDX (**1**).

Preparation of TFM-RDX (1). Young et al. have reported the preparation of TFM-RDX (**1**) via the following sequence (the only reported preparation of this compound),⁵² involving dehydration of commercially available trifluoroacetaldehyde hydrate to generate trifluoroacetaldehyde gas, which reacts with liquefied ammonia at low temperature. Upon warming, the hemiaminal intermediate is formed and then azeotropically dehydrated with benzene to produce hexahydro-2,4,6-tris(trifluoromethyl)-1,3,5-triazine intermediate, which is subsequently nitrated by nitrogen tetroxide and then nitrolyzed with nitric acid–trifluoroacetic anhydride (TFAA) mixture.

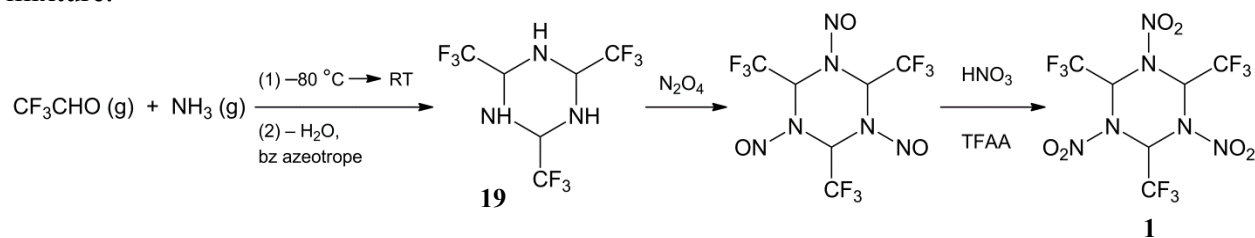


Figure 5. Literature synthesis of TFM-RDX (**1**)⁵²

Overall, this sequence has some aspects that are synthetically unattractive. These include a requirement for generation and handling of anhydrous trifluoroacetaldehyde gas as well as ammonia gas. In the final step, the mixture of nitric acid plus TFAA is potentially hazardous, having been reported to undergo unexpected and unexplained detonations.⁵³ Therefore, several variations on the fundamental reactions of this sequence were investigated as potentially superior alternatives. Reactions that were attempted in order to prepare the first intermediate, hexahydro-2,4,6-tris(trifluoromethyl)-1,3,5-triazine (**19**), utilizing commercially available derivatives of trifluoroacetaldehyde along with various ammonia equivalents are summarized below in Figure 6.

⁵¹ Dmowski, W.; Koliński, R.A. *Pol. J. Chem.* **1978**, 52, 547.

⁵² Young, J.A.; Schmidt-Collerus, J.J.; Krimmel, J.A. *J. Org. Chem.* **1971**, 36, 347.

⁵³ Bedford, C.D. *Chem. Eng. News* **1980**, 58(35), 33, 43.

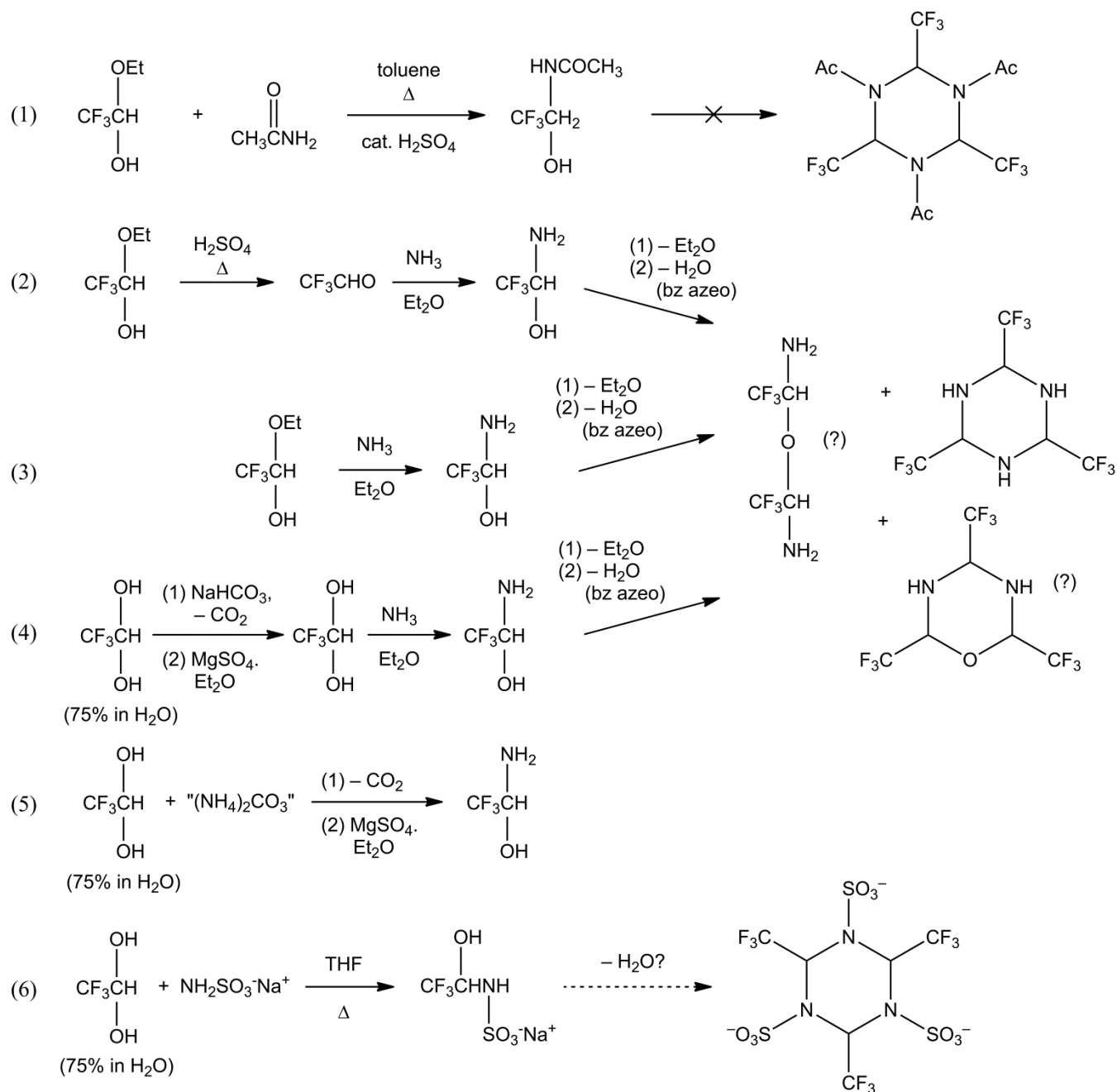


Figure 6. Reaction attempts to prepare TFM-RDX precursors

These included the following specific variations:

(1) A reaction analogous to the formation of 1,3,5-triacylhexahydro-1,3,5-triazines from alkanamides and formaldehyde, reported by Coon,⁵⁴ was attempted using trifluoroacetaldehyde monoethyl hemiacetal instead of formaldehyde. Krimmel et al. have reported that the reaction of trifluoroacetaldehyde with acetamide makes the corresponding aminal, 1,1-bisacetamido-2,2,2-

⁵⁴ Coon, C.L. *U.S. Patent 3,954,750* (1976).

trifluoroethane, but no triazine was mentioned as a product.⁵⁵ Likewise, we saw evidence of the expected initial intermediate, the known hemiaminal adduct between trifluoroacetaldehyde and acetamide (2,2,2-trifluoro-1-hydroxyacetamide)⁵⁶ but no evidence of the desired triazine.

(2) Trifluoroacetaldehyde monoethyl hemiacetal was used as an anhydrous source of trifluoroacetaldehyde gas (via acidic deprotection), which was introduced into ammonia in diethyl ether solvent. Following removal of ether solvent and azeotropic drying with benzene, benzene solvent was distilled off, the product was redissolved in hexanes and cooled to $-20\text{ }^{\circ}\text{C}$, and some crystals formed. An attempt was made to sublime the solid; benzene was retained in the sublimate, which contained some of the desired triazine product apparent by ^1H and ^{19}F NMR analysis, but the mixture was complex. This behavior may be consistent with coupling of the initial hemiaminal (1-amino-2,2,2-trifluoroethanol) in ways that lead to ether linkages that cannot cyclize to the desired triazine, some of which are suggested in Figure 6.

(3) Trifluoroacetaldehyde monoethyl hemiacetal was used directly as the reactant with ammonia. The reaction was carried out otherwise as in example (2) with similar results, although the hexanes-precipitated solid appeared relatively cleaner by NMR, but sublimation still did not effect purification.

(4) Trifluoroacetaldehyde hydrate (75% in water) was dried to “pure” hydrate by treatment with sodium bicarbonate (to remove acidic impurities) followed by drying with magnesium sulfate in diethyl ether, according to the procedure of Alimardanov et al.⁵⁷ This purified trifluoroacetaldehyde hydrate was used as the reactant in a reaction otherwise similar to example (3). Several runs under these conditions were carried out, sometimes producing the desired triazine in the product mixture but behaving somewhat irreproducibly in this regard.

(5) To commercial trifluoroacetaldehyde hydrate (75% in water) was added commercial ammonium carbonate as an ammonia equivalent. Following effervescence, the solution was dried, according to the procedure of Alimardanov et al.,⁵⁷ with MgSO_4 in diethyl ether. This solution exhibited NMR evidence of the formation of the initial hemiaminal (1-amino-2,2,2-trifluoroethanol) formed under other conditions in the previous examples.

(6) One potentially useful variation used sodium sulfamate as a “protected” form of ammonia in a reaction with trifluoroacetaldehyde hydrate (75% in water) in tetrahydrofuran solvent at reflux temperature. This reaction formed a product consistent by NMR with the expected initial hemiaminal, sodium 2,2,2-trifluoro-1-hydroxyethanesulfamate, though no evidence of a triazine was seen under these conditions. This intermediate offers the prospect that its dehydration might generate hexahydro-2,4,6-tris(trifluoromethyl)-1,3,5-triazine-1,3,5-trisulfonate, a potentially attractive precursor to TFM-RDX (**1**) that would be superior to the N-unsubstituted triazine (which requires intermediate nitrosation). The C-unsubstituted analog, hexahydro-1,3,5-triazine-1,3,5-trisulfonate, is a known direct precursor to RDX.⁵⁸

Following the complications encountered in these variations attempting to utilize more-convenient forms of trifluoroacetaldehyde and ammonia reactants, it was eventually decided to generate the simple reagents—as Young et al. had done⁵²—and carry out the initial steps of the sequence as they reported. In the course of doing so, an unexpected, interesting by-product was

⁵⁵ Krimmel, J.A.; Schmidt-Collerus, J.J.; Young, J.A.; Bohner, G.E.; Gray, D.N. *J. Org. Chem.* **1971**, *36*, 350.

⁵⁶ Gagosz, F.; Zard, S.Z. *Org. Synth.* **2007**, *84*, 32.

⁵⁷ Alimardanov, A.; Schmid, J.; Afragola, J.; Khafizova, G. *Org. Proc. Res. Dev.* **2008**, *12*, 424.

⁵⁸ Binnie, W.P.; Cohen, H.L.; Wright, G.F. *J. Am. Chem. Soc.* **1950**, *72*, 4457.

formed along with the desired triazine intermediate (as well as other by-products, such as ether-linked species that were speculated earlier): the corresponding eight-membered ring, octahydro-2,4,6,8-tetrakis(trifluoromethyl)-1,3,5,7-tetrazocine, which was isolated and confirmed by X-ray crystallography (Figure 7). No similar N-unsubstituted octahydro-1,3,5,7-tetrazocine has been reported as prepared and definitively identified, although the corresponding nonfluorinated derivative, octahydro-2,4,6,8-tetramethyl-1,3,5,7-tetrazocine, has been claimed in a Japanese patent to be formed from a reaction between acetaldehyde and ammonia, but without definitive characterization of the claimed product.⁵⁹ In contrast, the acetaldehyde–ammonia reaction has been thoroughly studied by many other researchers,⁶⁰ under many conditions, and a tetrazocine product has never been identified or mentioned. (The 1967 Japanese patent⁵⁹ has never been cited in chemical literature.) Our new tetrazocine intermediate offers the prospect of formation of a polyfluorinated HMX analog, “TFM-HMX,” with higher density than TFM-RDX albeit with the same fluorine content. Conditions for formation of the tetrazocine as an alternative product of the trifluoroacetaldehyde–ammonia reaction have not been optimized. The pursuit of TFM-RDX (**1**) remained the objective, although a mixture of cyclic intermediates (triazine and tetrazocine) leading to a mixture of corresponding nitramines could have been as useful for the purpose of testing agent defeat by this class of explosive, polyfluorinated nitramines.

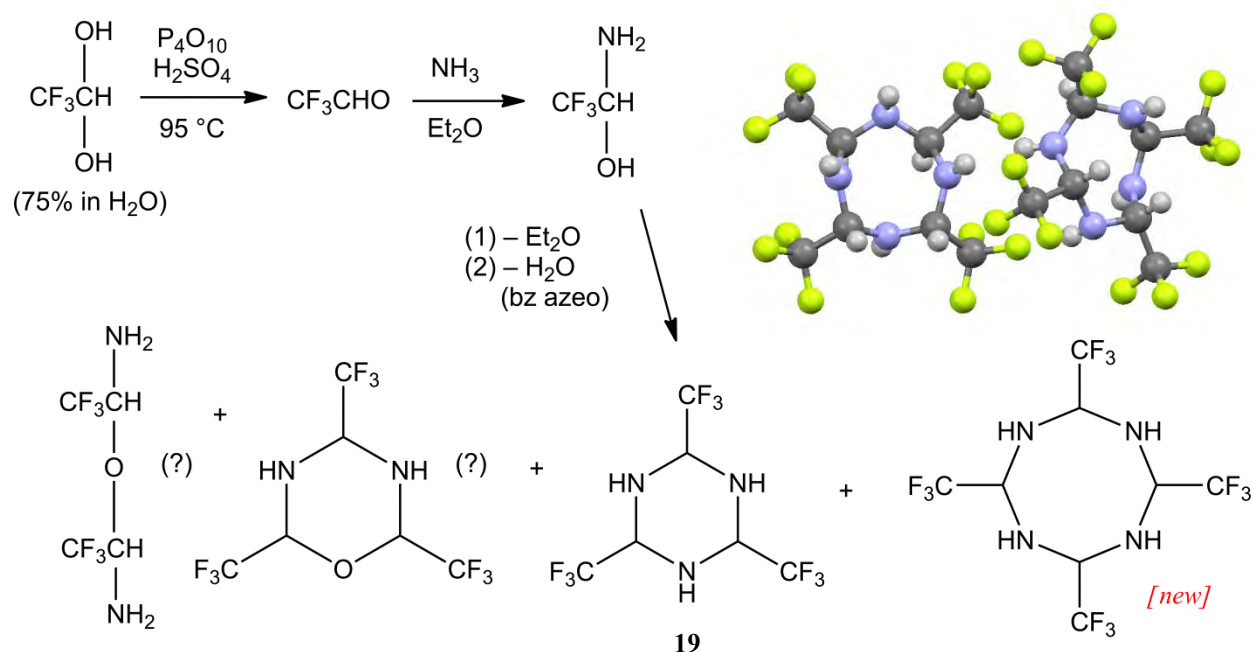


Figure 7. Preparation of perhydro(trifluoromethyl) –triazine (**19**) and -tetrazocine derivatives

In order possibly to avoid the intermediate trinitroso derivative as an additional step in the sequence (Figure 5), a direct N-nitration of intermediate **19** would have been preferable and was pursued. Initially, samples of crude intermediate **19** itself—available from the initial process

⁵⁹ Miyama, H. *Jpn. Tokyo Koho* JP S42-004262 B4 (1967).

⁶⁰ Nielsen, A.T.; Atkins, R.L.; Moore, D.W.; Scott, R.; Mallory, D.; LaBerge, J.M. *J. Org. Chem.* **1973**, 38, 3288; and references therein.

studies of its preparation—were used to test the feasibility of nitration procedures. The first method chosen was based on an analogous direct N-nitration of the amine nitrogens in a different N,N'-unprotected amination, octahydroimidazo[4,5-*d*]imidazole-2-one (Figure 8).⁶¹

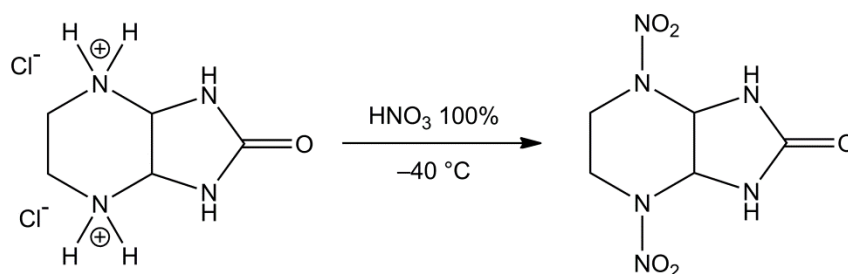


Figure 8. Direct N-nitration of a C-functionalized amination⁶¹

A similar attempt to directly nitrate hexahydrotriazine **19** with 98~100% nitric acid at $-30\text{ }^{\circ}\text{C}$ led to a reaction mixture showing increased complexity in its ^1H and ^{19}F NMR spectra after 6 days of reaction (nitramine **1** should be expected to be stable in nitric acid at low temperature). More importantly, the mixture's ^{14}N NMR spectra showed no evidence of an NO_2 absorption in the chemical shift region expected for a derivative of RDX (whose ^{15}N shift—expectedly equivalent to ^{14}N —occurs at $\delta -32.9$ vs. CH_3NO_2 , while other aliphatic secondary nitramines absorb in the range of $\delta -22.0$ to -34.7),⁶² even after additional reaction at $-12\text{ }^{\circ}\text{C}$ for 2 days and at ambient temperature for 5 days. It may be surmised that the fairly strongly acidic conditions were too harsh for the potentially sensitive hexahydrotriazine ring structure—as simple hexahydro-2,4,6-trimethyl-1,3,5-triazine (i.e., with CH_3 instead of CF_3) is known to be⁶³—probably involving ring cleavage reactions.

Attempts were made to nitrate **19** with a nonacidic nitrating reagent: the system tetra-*n*-butylammonium nitrate–trifluoromethanesulfonic (triflic) anhydride in dichloromethane, which generates nitronium triflate ($\text{NO}_2^+\text{CF}_3\text{SO}_3^-$) under anhydrous conditions and has been successfully used to N-nitrate various amines, amides, and imides.⁶⁴ Attempts using this nitrating reagent on crude **19** led to fairly complex mixtures—similar to those from the use of cold nitric acid—even in a run conducted in the presence of solid sodium sulfate as a potential acid scavenger in the organic solvent. This reaction quenched into aqueous sodium bicarbonate and extracted into dichloromethane showed a product mixture with multiple broad absorptions in the ^1H NMR spectrum, consistent with multiple NH sites either from degraded ring structures or more than one asymmetric hexahydrotriazine, i.e., with partial NH and partial N-substitution. It was tentatively surmised that the stoichiometric triflic acid generated upon partial N-nitration of sites in reactant **19** could introduce complications, either ring cleavage or nitrogen protonation hindering N-nitration. For this reason, a still less acidic nitrating system might have been preferable.

⁶¹ Ramakrishnan, V.T.; Vedachalam, M.; Boyer, J.H. *Heteroatom Chem.* **1991**, 2, 669.

⁶² Bulusu, S.; Axenrod, T.; Autera, J.R. *Org. Magn. Reson.* **1981**, 16, 52.

⁶³ Delepine, M. *Comp rend.* **1907**, 144, 853.

⁶⁴ Adams, C.M.; Sharts, C.M.; Shackelford, S.A. *Tetrahedron Lett.* **1993**, 34, 6669.

The system tetra-*n*-butylammonium nitrate (TBAN)–trifluoroacetic anhydride (TFAA) in dichloromethane has been used for various C-nitrations of organics,⁶⁵ although not reportedly for N-nitrations to nitramines. (A similar system, ammonium nitrate–trifluoroacetic anhydride—Crivello’s reagent—has been used for various N-nitrations but requires a polar solvent such as nitromethane, and the yield of RDX from nitrolysis of 1,3,5-triacetylhexahydro-1,3,5-triazine using this system was only 8%,⁶⁶ although removal of *N*-acetyl protecting groups might be expected to be more difficult than simple nitration of NH sites.) The ring structure of **19** should be more tolerant of trifluoroacetic acid by-product from N-nitration by this reagent system than of stronger acids generated by the other reagents tried. Also, the reactive trifluoroacetyl nitrate [CF₃CO(ONO₂)] intermediate formed by the reagent should be sufficiently powerful to nitrate the less-nucleophilic amine sites of **19**, unlike acetyl nitrate, for example.

However, in testing this nitrating reagent, it was decided to use a purer and less valuable substrate as a model reactant: the trifluoromethyl-substituted aminated 2-(trifluoromethyl)imidazolidine (**20**), a known, readily purified compound straightforwardly prepared from ethylenediamine plus trifluoroacetaldehyde hydrate.⁶⁷ It was discovered that a twofold excess of nitrating reagent (TBAN–TFAA) was potentially useful, producing after 3 days at ambient temperature two predominant species (68:32 mole-ratio) that were consistent by ¹H and ¹⁹F NMR with species such as the di- and mono-*N*-nitro derivatives of **20**, respectively. The ¹⁴N NMR spectrum of the reaction mixture showed a broad absorption at δ –32, consistent with secondary nitramine but possibly containing both *N*-nitro derivatives.

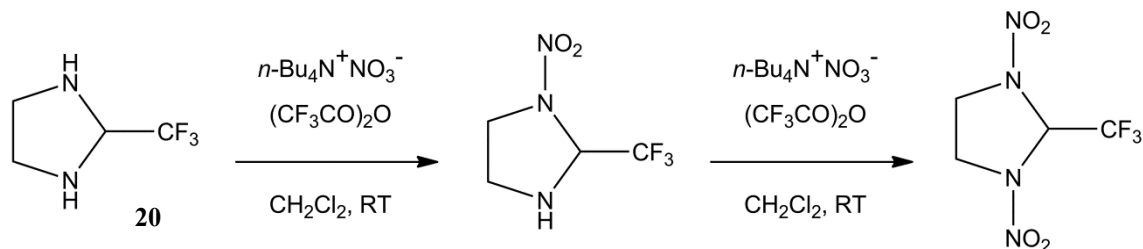


Figure 9. “Nonacidic” nitration of a model reactant, 2-(trifluoromethyl)imidazolidine (**20**)

Ultimately, however, workup of the reaction produced no isolable species consistent with the desired bisnitramine derivative of **20**. Some light was shed on this apparent failure of nitration from consideration of conclusions drawn from a thorough investigation of the behavior of nitrate salt–trifluoroacetic anhydride nitrating reagents, by Vilarrasa and co-workers.⁶⁸ Their studies of the stability of such nitrating reagents strongly suggest that N-nitrations, if feasible, ought to occur within hours, at most, as such systems are not very stable for days at ambient temperatures.

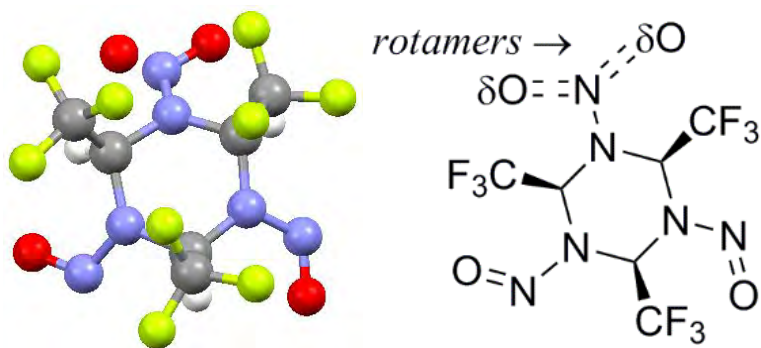
⁶⁵ Njoroge, F.G.; Vibulbhan, B.; Pinto, P.; Chan, T.-M.; Osterman, R.; Remiszewski, S.; Del Rosario, J.; Doll, R.; Girijavallabhan, V.; Ganguly, A.K. *J. Org. Chem.* **1998**, *63*, 445.

⁶⁶ Suri, S.C.; Chapman, R.D. *Synthesis* **1988**, 743.

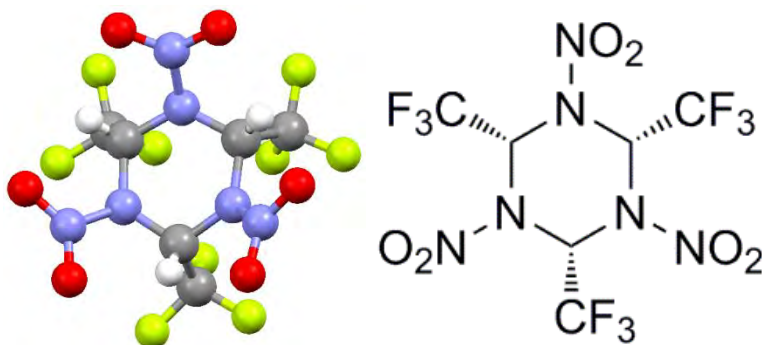
⁶⁷ Crank, G.; Harding, D.R.K.; Szinai, S.S. *J. Med. Chem.* **1970**, *13*, 1212.

⁶⁸ Romea, P.; Aragones, M.; Garcia, J.; Vilarrasa, J. *J. Org. Chem.* **1991**, *56*, 7036.

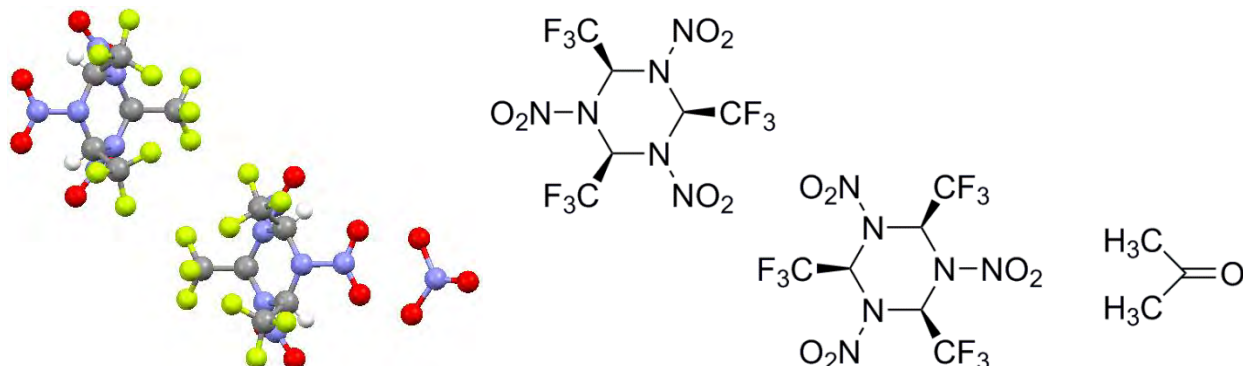
Thus, it was decided to prepare TFM-RDX (**1**) essentially following the procedure described by Young et al.⁵² (Figure 5). The only significant deviation from their procedure that was employed was to recrystallize TFM-RDX from cyclopentane instead of cyclohexane in order to maintain a lower temperature, in hopes of avoiding any thermal degradation of the product. In the course of carrying out this sequence, key compounds—though known from that prior study—were newly characterized crystallographically (Figure 10), including intermediate hexahydro-1,3,5-trinitroso-2,4,6-tris(trifluoromethyl)-1,3,5-triazine (density $\rho = 1.964 \text{ g/cm}^3$) and TFM-RDX (density $\rho = 2.006 \text{ g/cm}^3$, slightly lower than that predicted by analogy to a similar bicyclo-HMX derivative, *vide supra*). TFM-RDX exhibited a complication during preparation of some samples in that it readily formed crystalline adducts with certain solvents, including acetone, which was discovered by crystallographic analysis. (Subsequent avoidance of acetone in its workup alleviated that complication.) Another interesting adduct was discovered from analysis of a crystal retrieved from the mother liquor of one recrystallization, which proved to be an adduct of TFM-RDX with 2,2,2-trifluoro-1-nitraminoethanol [$\text{CF}_3(\text{NHNO}_2)\text{CHOH}$], obviously formed during the nitration step by reaction of a minor amount of residual 1-amino-2,2,2-trifluoroethanol—a known intermediate (Figure 6) in the sequence leading to hexahydro-2,4,6-tris(trifluoromethyl)-1,3,5-triazine (**19**)—that carried through the sequence without cyclization.



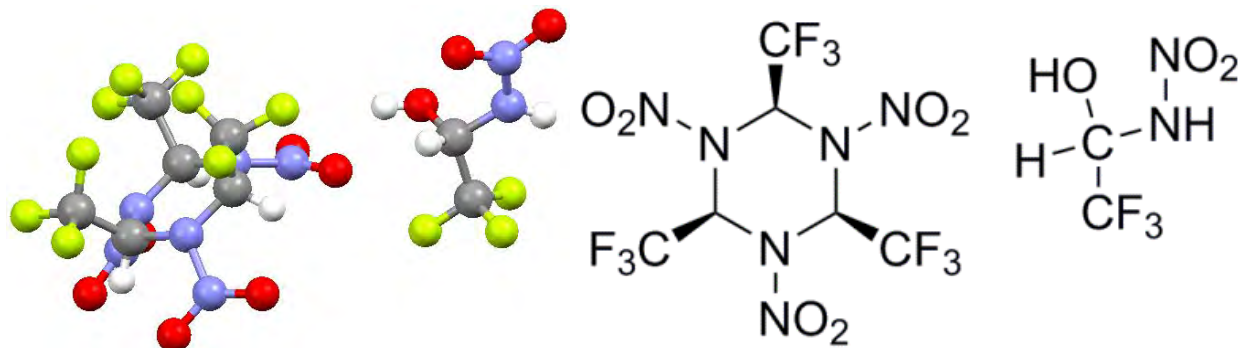
(a) Hexahydro-1,3,5-trinitroso-2,4,6-tris(trifluoromethyl)-1,3,5-triazine; $\rho = 1.964 \text{ g/cm}^3$.



(b) Hexahydro-1,3,5-trinitro-2,4,6-tris(trifluoromethyl)-1,3,5-triazine (TFM-RDX); $\rho = 2.006 \text{ g/cm}^3$.



(c) TFM-RDX adduct (2:1) with acetone; $\rho = 1.866 \text{ g/cm}^3$.



(d) TFM-RDX adduct with 2,2,2-trifluoro-1-nitraminoethanol; $\rho = 2.004 \text{ g/cm}^3$.

Figure 10. Crystallographic structures of compounds of interest related to TFM-RDX

TFM-RDX formulation. For the specific application of agent defeat testing to be conducted collaboratively at NSWC Indian Head, it was decided to test the sporicidal efficacy of a new PBX formulation based on TFM-RDX in comparison to PBXN-5, the standard booster charge employed in their apparatus.¹ The preferable test formulation would therefore be similar in composition to PBXN-5 (95.0% HMX + 5.0% vinylidene fluoride–hexafluoropropylene copolymer, such as Viton A) but with TFM-RDX replacing some of the HMX in order to maximize the relative amount of biocidal hydrogen fluoride detonation product—similar to the conceptual analysis described above for a simple binary RDX–TFM-RDX formulation. The vinylidene fluoride–hexafluoropropylene copolymer used in this study was 3M™ product Fluorel™ FC-2175 (functionally equivalent to DuPont Viton® A), which consists of 60.0 wt% (77.8 mol%) vinylidene fluoride monomer (CH₂=CF₂) and 40.0 wt% (22.2 mol%) hexafluoropropylene monomer (CF₃CF=CF₂).⁶⁹

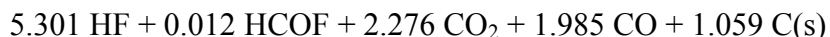
Taking into account the hydrogen and fluorine content of the Fluorel™ FC-2175, a ternary composition that balances hydrogen and fluorine (in order to maximize hydrogen fluoride product upon detonation) is calculated as:

- 60.5 wt% TFM-RDX (C₆H₃F₉N₆O₆)
- 34.5 wt% HMX (C₄H₈N₈O₈)
- 5.0 wt% Fluorel™ FC-2175 [(C₃F₆)_{0.222}(C₂H₂F₂)_{0.778}]_n

The empirical formula of this composition (per mole) could conceptually undergo detonation to produce the following simplified reaction:



More realistically, calculations of explosive performance by Cheetah 7.0 predict the following products of detonation of this formulation:



However, the minor by-product formyl fluoride (HCOF) is known not to be highly stable, being susceptible to either spontaneous unimolecular or hydrolytic degradation to form hydrogen fluoride as a final, stable product.⁷⁰ The final product composition with 5.313 moles of hydrogen fluoride per “mole” of formulation contains 28.9 wt% hydrogen fluoride, the maximum content achievable by a ternary formulation of these three ingredients, also produced under detonation conditions, thus hopefully serving as a superior sporicide against anthrax or its surrogates.

Prior to its formulation into a PBX, safety properties of TFM-RDX needed to be measured. It was found that it is a highly insensitive explosive, with test results as follow, all measured in accordance with AOP-7 Edition 2. Impact sensitivity (ERL/Bruceton Impact Test Category US/201.01.001, modified Type 12 tooling, 2.5-kg weight): TFM-RDX 10/10 no-fires at 200 cm; RDX *H*₅₀ = 18 cm. Friction sensitivity (ABL Sliding Friction Category US/201.02.005): TFM-RDX 20/20 no-fires at 1000 lbf; PETN low-fire 200 lbf. Electrostatic sensitivity (NAWC/NSWC Method ESD Category US/201.03.002/003): TFM-RDX 20/20 no-fires at 0.25 J; RDX

⁶⁹ [http://multimedia.3m.com/mws/mediawebserver?](http://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSuH8gc7nZxtU5Y_1OxTSevUqe17zHvTSevTSeSSSSSS-&fn=FluorelFluoroelastomerFC-2175_Ce)

[mwsId=SSSSSuH8gc7nZxtU5Y_1OxTSevUqe17zHvTSevTSeSSSSSS-&fn=FluorelFluoroelastomerFC-2175_Ce](http://multimedia.3m.com/mws/mediawebserver?mwsId=SSSSSuH8gc7nZxtU5Y_1OxTSevUqe17zHvTSevTSeSSSSSS-&fn=FluorelFluoroelastomerFC-2175_Ce)

⁷⁰ Nesmejanow, A.N.; Kahn, E.J. *Berichte der Deutschen Chemischen Gesellschaft [Abteilung] B: Abhandlungen* **1934**, 67B, 370.

20/20 no-fires at 0.25 J. DSC ($2\text{ }^{\circ}\text{C min}^{-1}$ per ASTM E537) peak: $180\text{ }^{\circ}\text{C}$.

With these attractive sensitivity properties determined for TFM-RDX, a molding powder was prepared with the calculated “ideal” composition (*vide supra*), which was locally designated “TFM-PBX-5” (by analogy to PBXN-5). This formulation, even containing HMX, still showed adequate sensitivity properties. Impact sensitivity (ERL/Bruceton Impact Test Category US/201.01.001, modified Type 12 tooling, 2.5-kg weight): TFM-PBX-5 $H_{50} = 34\text{ cm}$; RDX $H_{50} = 18\text{ cm}$. Friction sensitivity (ABL Sliding Friction Category US/201.02.005): TFM-PBX-5 20/20 no-fires at 1000 lbf; PETN low-fire 200 lbf. Electrostatic sensitivity (NAWC/NSWC Method ESD Category US/201.03.002/003): TFM-PBX-5 20/20 no-fires at 0.25 J; RDX 20/20 no-fires at 0.25 J.

The molding powder was pressed with a $\frac{1}{2}$ -inch die under high pressure into four pellets (~ 3.26 grams each) with dimensions that would be accommodated by the inner core of the booster charge container that NSWC Indian Head uses in their test apparatus (Figure 11): $0.500''$ dia. $\times \sim 0.557''$ length.



Figure 11. Sample container for booster charge

Following two preliminary shots of one pellet each in order to ensure initiation of detonation, sporicidal efficacy against anthrax surrogate spores would be determined using two other pellets and compared to the performance of PBXN-5 baseline formulation. Although the physical tests have been conducted at NSWC Indian Head at the time of this report, their data reduction has not been completed. Therefore, final results of the testing from this project will need to be reported by NSWC Indian Head at a future time.

Syntheses and characterization data

Octahydro-2,4,6,8-tetrakis(trifluoromethyl)-1,3,5,7-tetrazocine. Trifluoroacetaldehyde hydrate solution (13 mL, 75% in water, Oakwood Products) was added dropwise over 1.5 h to a mixture of P_4O_{10} (8 g) in conc. H_2SO_4 (20 mL). The effluent gases generated were transferred via Teflon tubing to a trap cooled in a dry ice–acetone bath. After the addition of hydrate, the heating was continued another 30 min, after which approximately 7–8 mL of CF_3CHO had been collected in the trap. In a separate flask, liquefied ammonia ($\sim 15\text{ mL}$) was collected at dry ice–acetone temperature, and then diethyl ether (100 mL) was added cold, along with a stirbar. The liquefied CF_3CHO was allowed to slowly warm to room temperature over $\sim 45\text{ min}$, as the gas transferred via Teflon tubing into the ammonia solution kept cold in a dry ice–acetone bath. Once CF_3CHO transfer was complete, the cooling bath was removed, and excess NH_3 was allowed to evaporate. Diethyl ether was distilled out by heating with a $60\text{ }^{\circ}\text{C}$ oil bath; when distillation appeared complete, the mixture was cooled to room temperature, and house vacuum

was applied for 5–10 min to remove most of the Et₂O. The reaction's mass at this time was 10.79 g. The product oil was left overnight at room temperature.

The next day, 25 mL of benzene was added; the mixture became cloudy and a water phase was present. The mixture was refluxed with a Dean–Stark trap (of 20 mL volume, containing 20 mL benzene initially introduced) in place. After 6 h, water collection appeared complete, with 1.6 mL present. Benzene was distilled off at atmospheric pressure using a 100 °C oil bath. After cooling the pot to room temperature, house vacuum was applied for 10 min to remove any residual benzene, leaving a white semisolid residue weighing 8.3 g. Carbon tetrachloride (20 mL) was added and gently heated to make a solution. Upon cooling to room temperature, some crystals precipitated. The crystals (1.4 g) which were filtered off melted over a broad range of 60–95 °C. ¹H NMR analysis of these crystals clearly showed benzene still present. Their ¹⁹F NMR showed a major doublet at δ –79.9, a minor doublet at δ –80.8, and other smaller doublets. CCl₄ was distilled from the filtrate at atmospheric pressure. The residue's ¹⁹F NMR showed a major doublet at δ –80.92 and minor doublets at δ –81.6, –79.9, –75.6. The residue was sublimed under house vacuum (~10 torr) with the condenser cooled by dry ice–acetone. Some material was collected without applying any heat, so the apparatus was disassembled, and the condenser was washed with Et₂O into a flask. Then a second sublimation was conducted using 40 °C heat; two fractions were collected at this temperature. There still remained a semisolid in the pot of the sublimation apparatus.

After standing several weeks, the fractions were reexamined: Et₂O had evaporated; from the third fraction, nicely formed cubic crystals were present. X-ray crystallographic analysis of one of these showed it to be the tetrazocine structure rather than the expected triazine. The residue from the sublimation pot was dissolved in Et₂O; the solution was allowed to evaporate, and this deposited more crystals, which were presumed to be more of the tetrazocine product, of which there was approximately 1–2 g. ¹H NMR (CDCl₃) δ 2.0 (t, 2 H), 2.3 (t, 2 H), 4.6 (m, 4 H); ¹⁹F NMR (CDCl₃) δ –79.9 (d); ¹³C NMR (CDCl₃) δ 67.93 (q, *J* = 32.1 Hz), 123.69 (q, *J* = 281.8 Hz). The crude product still contained impurities according to minor peaks in the NMR spectra and consistent with a broad m.p. (97 °C) by DSC.

Hexahydro-2,4,6-tris(trifluoromethyl)-1,3,5-triazine. The crude product from a separate reaction—conducted similarly to that described above—was subjected to vacuum distillation (10 torr). Several fractions were collected, but the major one distilled over 52–80 °C. ¹⁹F NMR analysis of this fraction showed three doublets: δ –81.6, –80.9 (major), –75.6. This liquid was stored at –20 °C for a day, which caused the entire contents to solidify. On warming to room temperature, there was a supernatant liquid along with some crystalline precipitate, which was filtered off. The white solid could be recrystallized by CCl₄ to give fine colorless needles. ¹H NMR (CDCl₃) δ 1.9 (m, 3 H), 4.2 (m, 3 H); ¹⁹F NMR (CDCl₃) δ –80.9 (d); ¹³C (CDCl₃) δ 69.53 (q, *J* = 33.3 Hz), 122.47 (q, *J* = 279.4 Hz). M.p. (DSC) 85 °C (lit.⁵² 83–84 °C).

Hexahydro-1,3,5-trinitroso-2,4,6-tris(trifluoromethyl)-1,3,5-triazine. This intermediate was prepared following the procedure of Young et al.⁵²

Hexahydro-1,3,5-trinitro-2,4,6-tris(trifluoromethyl)-1,3,5-triazine (TFM-RDX). This product was prepared following the procedure of Young et al.,⁵² except that it was recrystallized from cyclopentane instead of cyclohexane.

Personnel Supported

Personnel supported by this project, beyond the Principal Investigator, are listed as co-authors of this report: Drs. Matthew C. Davis and Thomas J. Groshens, Chemistry Branch (Code 4L4200D), NAWCWD; Kristin J. Hall and Que T. Bui-Dang, Synthesis and Formulations Branch (Code 474100D), NAWCWD; Richard A. Khouri and John P. Carroll, Safe-Arm Development Branch (Code 478300D), NAWCWD. Support for all of them was to a minor extent of time.

Publications

Robert D. Chapman, Suhithi M. Peiris, “Candidate Energetic Materials for ‘Halogenated Explosives to Defeat Biological Agents’”, 1 Nov 2012; ADB387261 (Distribution Statement C. Distribution authorized to U.S. Government Agencies and their contractors; Administrative or Operational Use).

Interactions/Transitions

Presentations: “Halogenated Explosives to Defeat Biological Agents” Robert D. Chapman, *DTRA Basic Research Technical Review* (Springfield, VA), 26 July 2012; *DTRA Basic Research Technical Review* (Springfield, VA), 25 July 2013.

New discoveries, inventions, or patent disclosures

“Octafluoropentaerythrityltetramine (Octafluoro-PETA) and Process For Its Preparation” Robert D. Chapman, Richard A. Hollins, *U.S. Patent* 8,008,527 (2011).

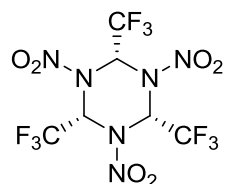
“Process for Employing HNFX as a Biocidal Explosive” Robert D. Chapman, *U.S. Patent* 8,221,566 (2012).

Synthesis of a new compound, octahydro-2,4,6,8-tetrakis(trifluoromethyl)-1,3,5,7-tetrazocine, potentially useful as a precursor to new fluorinated explosives.

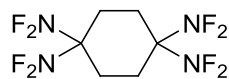
New characterizations of highly fluorinated explosive TFM-RDX.

Table 3. Solid fluorinated energetic material candidates and some properties

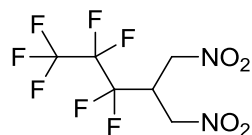
<u>Structure</u> <u>(No.) Empirical formula</u> <u>Chemical name</u> <u>Literature reference</u>	<u>wt% Fluorine</u>	<u>Oxygen balance</u> $\Omega(\text{CO}_2)$	<u>m.p. (°C)</u>	<u>b.p. (°C)/P(torr)</u>	$\Delta H_{\text{vap}}^{\text{theor}}$ (kJ/mol)	$\Delta H_{\text{f}}^{\text{theor}}$ (kJ/mol) ^a
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(1) $\text{C}_6\text{H}_3\text{F}_9\text{N}_6\text{O}_6$ 40.13% -11.3% 118° 79.22 -1912
 Hexahydro-1,3,5-trinitro-2,4,6-tris(trifluoromethyl)-1,3,5-triazine [2,4,6-Tris(trifluoromethyl)RDX, TFM-RDX]
Ref: Young, J.A.; Schmidt-Collerus, J.J.; Krimmel, J.A. *J. Org. Chem.* **1971**, 36, 347.



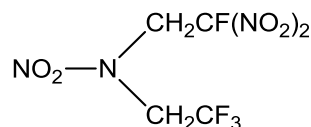
(2) $\text{C}_6\text{H}_8\text{F}_8\text{N}_4$ 52.75% -66.6% 108° 46.78 -217
 1,1,4,4-Tetrakis(difluoramino)cyclohexane
Ref: Dinwoodie, A.H.; Grigov, J. *GB Patent* 1134541 (1968).
Note: High sensitivity (primary explosive); synthesis is not practically scalable.



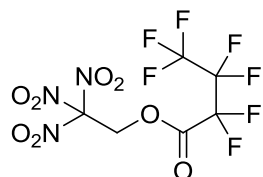
(3) $\text{C}_6\text{H}_5\text{F}_7\text{N}_2\text{O}_4$ 44.02% -37.1% 62° 49.60 -1627
 1,1,1,2,2,3,3-Heptafluoro-5-nitro-4-(nitromethyl)pentane
Ref: Cook, D.J.; Pierce, O.R.; McBee, E.T. *J. Am. Chem. Soc.* **1954**, 76, 83.
Note: Melting point is too low to qualify for solid explosive formulations under NAVSEAINST 8020.5C.

^a Estimated as $\Delta H_{\text{f}}^{\text{theor}}(\text{solid}) \sim \Delta H_{\text{f}}^{\text{theor}}(\text{gas}) - \Delta H_{\text{vap}}^{\text{theor}}$

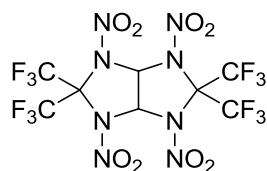
<u>Structure</u> <u>(No.) Empirical formula</u> <u>Chemical name</u> <u>Literature reference</u>	<u>wt% Fluorine</u>	<u>Oxygen balance</u> $\Omega(\text{CO}_2)$	<u>m.p. (°C)</u>	<u>b.p. (°C)/P(torr)</u>	$\Delta H_{\text{vap}}^{\text{theor}}$ (kJ/mol)	$\Delta H_{\text{f}}^{\text{theor}}$ (kJ/mol) ^a
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(4) C ₄ H ₄ F ₄ N ₄ O ₆	27.13%	-11.4%	61°		56.40	-879
<i>N</i> -(2-Fluoro-2,2-dinitroethyl)- <i>N</i> -(2,2,2-trifluoroethyl)nitramine						
Ref: Witucki, E.F.; Rowley, G.L.; Ogimachi, N.N.; Frankel, M.B. <i>J. Chem. Eng. Data</i> 1971 , 16, 373.						
Note: Melting point is too low to qualify for solid explosive formulations under NAVSEAINST 8020.5C.						



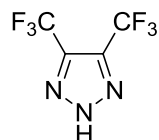
(5) C ₆ H ₂ F ₇ N ₃ O ₈	35.27%	-6.4%	39°		44.51	-1449
2,2,2-Trinitroethyl heptafluorobutyrate						
Ref: Conly, J.C. <i>U.S. Patent</i> 3160654 (1964).						
Note: Melting point is too low to qualify for solid explosive formulations under NAVSEAINST 8020.5C.						



(6) C ₈ H ₂ F ₁₂ N ₈ O ₈	40.27%	-8.5%	111°		95.14	-2121
Octahydro-1,3,4,6-tetranitro-2,2,5,5-tetrakis(trifluoromethyl)imidazo[4,5- <i>d</i>]imidazole [2,2,5,5-Tetrakis(trifluoromethyl)bicyclo-HMX]						
Ref: Koppes, W.M.; Chaykovsky, M.; Adolph, H.G.; Gilardi, R.; George, C. <i>J. Org. Chem.</i> 1987 , 52, 1113.						
Note: Synthesis is unwieldy; properties are similar to (1).						

^a Estimated as $\Delta H_{\text{f}}^{\text{theor}}(\text{solid}) \sim \Delta H_{\text{f}}^{\text{theor}}(\text{gas}) - \Delta H_{\text{vap}}^{\text{theor}}$

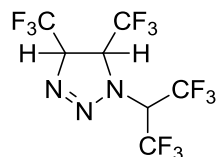
<u>Structure</u> <u>(No.) Empirical formula</u> <u>Chemical name</u> <u>Literature reference</u>	<u>wt% Fluorine</u>	<u>Oxygen balance</u> $\Omega(\text{CO}_2)$	<u>m.p. (°C)</u>	<u>b.p. (°C)/P(torr)</u>	$\Delta H_{\text{vap}}^{\text{theor}}$ (kJ/mol)	$\Delta H_{\text{f}}^{\text{theor}}$ (kJ/mol) ^a
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(7) $\text{C}_4\text{HF}_6\text{N}_3$ 55.59% -42.9% (solid) subl 40 °C/vac 40.12 -1090
4,5-Bis(trifluoromethyl)-2H-1,2,3-triazole

Ref: Michot, C.; Armand, M.; Gauthier, M.; Choquette, Y. *U.S. Patent* 6395367 (2002).

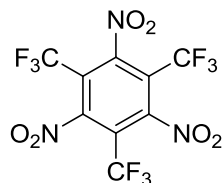
Note: Melting point is unreported but likely to be too low to qualify for solid explosive formulations under NAVSEAINST 8020.5C.



(8) $\text{C}_7\text{H}_3\text{F}_{12}\text{N}_3$ 63.84% -42.6% 56° 36.77 -2477
4,5-Dihydro-4,5-bis(trifluoromethyl)-1-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-1H-1,2,3-triazole
[4,5-Bis(trifluoromethyl)-1-hexafluoroisopropyl-1H-1,2,3-triazoline]

Ref: Fields, R.; Tomlinson, J.P. *J. Fluor. Chem.* **1979**, 14, 19.

Note: Melting point is too low to qualify for solid explosive formulations under NAVSEAINST 8020.5C.



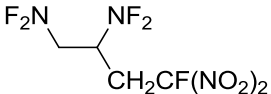
Unknown

(9) $\text{C}_9\text{F}_9\text{N}_3\text{O}_6$ 40.99% -28.8% 65.19^b -1813 (approx)^b
1,3,5-Trinitro-2,4,6-tris(trifluoromethyl)benzene

Note: An unreported compound, so a synthetic route needs to be developed.

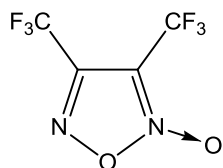
^a Estimated as $\Delta H_{\text{f}}^{\text{theor}}(\text{solid}) \sim \Delta H_{\text{f}}^{\text{theor}}(\text{gas}) - \Delta H_{\text{vap}}^{\text{theor}}$. ^b Using $\Delta H_{\text{vap}}^{\text{theor}}$ of 2,4,6-tri-*t*-butyl-1,3,5-trinitrobenzene

Table 4. Liquid fluorinated energetic material candidates and some properties

<u>Structure</u> <u>(No.) Empirical formula</u> <u>Chemical name</u> <u>Literature reference</u>	<u>wt% Fluorine</u>	<u>Oxygen balance</u> $\Omega(\text{CO}_2)$	<u>m.p. (°C)</u>	<u>b.p. (°C)/P(torr)</u>	$\Delta H_{\text{vap}}^{\text{theor}}$ (kJ/mol)	$\Delta H_{\text{f}}^{\text{theor}}$ (kJ/mol) ^a
$\text{CF}(\text{NO}_2)_2\text{OCH}_2\text{CF}_3$ (10) $\text{C}_3\text{H}_2\text{F}_4\text{N}_2\text{O}_5$ Fluorodinitromethyl 2,2,2-trifluoroethyl ether Ref: Kamlet, M.J.; Adolph., H.G.. <i>J. Org. Chem.</i> 1968 , 33, 3073.	34.22%	0%		45° / 15	37.04	−1032
$\text{CF}(\text{NO}_2)_2\text{CH}_2\text{OCF}_3$ (11) $\text{C}_3\text{H}_2\text{F}_4\text{N}_2\text{O}_5$ 2-Fluoro-2,2-dinitroethyl trifluoromethyl ether Ref: Peters, H.M.; Simon, R.L. Jr.; Ross, L.O.; Hill, M.E. <i>J. Chem. Eng. Data</i> 1975 , 20, 118.	34.22%	0%		51° / 35	37.88	−1079
$\text{CF}(\text{NO}_2)_2\text{CH}_2\text{CH}_2\text{CF}_3$ (12) $\text{C}_4\text{H}_4\text{F}_4\text{N}_2\text{O}_4$ 1,1,1,4-Tetrafluoro-4,4-dinitrobutane Ref: Bissell, E.R.; Fields, D.B. <i>Tetrahedron</i> 1970 , 26, 5737.	34.53%	−29.1%		155° / 742	40.72	−954
 (13) $\text{C}_4\text{H}_5\text{F}_5\text{N}_4\text{O}_4$ 3,4-Bis(difluoramino)-1-fluoro-1,1-dinitrobutane Ref: Fokin, A.V.; Nikolaeva, A.D.; Studnev, Yu.N.; Proshin, N.A. <i>Bull. Acad. Sci. USSR (Div. Chem. Sci.)</i> 1970 , 679.	35.43%	−23.9%		65° / 0.1	50.36	−354
$\text{CF}_3\text{CH}[\text{OCH}_2\text{C}(\text{NF}_2)_2\text{CH}_2\text{CH}_2\text{CF}(\text{NO}_2)_2]_2$ (14) $\text{C}_{12}\text{H}_{13}\text{F}_{13}\text{N}_8\text{O}_{10}$ Bis[2,2-bis(difluoramino)-5-fluoro-5,5-dinitropentyl]trifluoroacetal (SYTA) Ref: Frankel, M.B. <i>U.S. Patent</i> 4341712 (1982).	36.52%	−33.1%		(liquid)	85.76	−1649

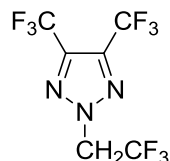
^a Estimated as $\Delta H_{\text{f}}^{\text{theor}}(\text{liquid}) \approx \Delta H_{\text{f}}^{\text{theor}}(\text{gas}) - \Delta H_{\text{vap}}^{\text{theor}}$

<u>Structure</u> <u>(No.) Empirical formula</u> <u>Chemical name</u> <u>Literature reference</u>	<u>wt% Fluorine</u>	<u>Oxygen balance</u> <u>$\Omega(\text{CO}_2)$</u>	<u>m.p. (°C)</u>	<u>b.p. (°C)/P(torr)</u>	<u>$\Delta H_{\text{vap}}^{\text{theor}}$ (kJ/mol)</u>	<u>$\Delta H_{\text{f}}^{\text{theor}}$ (kJ/mol)^a</u>
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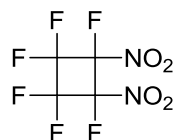
(15) C₄F₆N₂O₂ 51.34% -21.6% 88° 37.58 -1139
3,4-Bis(trifluoromethyl)furoxan

Ref: Krzhizhevskii, A.M.; Mirzabekyants, N.S.; Cheburkov, Yu.A.; Knunyants, I.L. *Bull. Acad. Sci. USSR (Div. Chem. Sci.)* **1974**, 2421.



(16) C₆H₂F₉N₃ 59.56% -47.4% 133° 41.30 -1750
2-(2,2,2-Trifluoroethyl)-4,5-bis(trifluoromethyl)-2H-1,2,3-triazole

Ref: Fields, R.; Tomlinson, J.P. *J. Fluor. Chem.* **1979**, 14, 19.



(17) C₄F₆N₂O₄ 44.87% -6.3% 62° / 100 46.26 -1150
Hexafluoro-1,2-dinitrocyclobutane

Ref: Knunyants, I.L.; Fokin, A.V. *Proc. Acad. Sci. USSR (Dokl. Chem.)* **1956**, 111, 731.

^a Estimated as $\Delta H_{\text{f}}^{\text{theor}}(\text{liquid}) \approx \Delta H_{\text{f}}^{\text{theor}}(\text{gas}) - \Delta H_{\text{vap}}^{\text{theor}}$

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